Equilibrium and Kinetic Studies on Halide Derivatives

of Malachite Green

III.   *p*-Fluoro-, *p*-Bromo- and *p*-Iodo-Malachite Green

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The series of investigations of protolytic and hydration equilibria and reaction rates of basic triphenylmethane dyes is continued with the investigation of *p*-Fluoro-, *p*-Bromo- and *p*-Iodo Malachite Green.

Three protolytic, two hydration and six rate constants of each dye have been determined by spectrophotometric measurements in aqueous solutions with the ionic strength 0.5 M at 20.0°C. A comparison with the values of the corresponding constants of Malachite Green and *p*-Chloro Malachite Green shows that there is no marked differences between Malachite Green and its para-halide derivatives in contrast with the great differences that were found between Malachite Green and its ortho-halide derivatives.

It was found in a previous investigation [1] that the *ortho*-bromo and *ortho*-iodo substituents in the dyes o-Bromo Malachite Green (*o*-BrMG) and *o*-Iodo Malachite Green (*o*-IMG) have a very strong influence on the hydration reactions and the hydration rates of these dyes. The bulky bromo- and iodo-substituents in the *ortho* position to the central methane carbon cause a very strong "steric hindrance". In order to show that it is really the position and not the nature of the substituents that is responsible for the great differences in the behaviour of Malachite Green (MG) and its *o*-bromo- and *o*-iodo-derivatives in this case, the corresponding *para*-derivatives have now been investigated.

A similar reaction scheme and the same symbols and definitions as in Ref.[1] have been used.

The expressions for the initial absorbancy

$$e_0 = \frac{e_B + hK_1 e_G}{1 + hK_1} \tag{1}$$
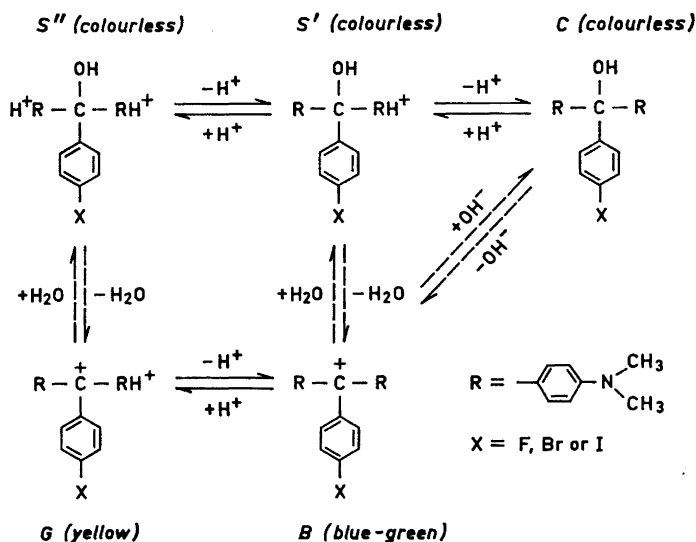
the equilibrium absorbancy

$$e_\infty = \frac{e_B + hK_1 e_G}{1 + 1/K_6 + K_4/hK_6 + hK_1(1 + K_2)} \qquad (2)$$

and the rate constant of the over-all reaction

$$k = \frac{k_2 h^2 + k_4 hK_3 + k_6 K_3 K_4}{h^2 + hK_3 + K_3 K_4} + \frac{k_1 hK_1 + k_3 + k_5 oh}{1 + hK_1} \qquad (3)$$

are also the same as in Ref.[1]

Since the very slightly soluble carbinols of *para*-Bromo and *para*-Iodo Malachite Green make the accurate measurements in weakly alkaline and even neutral aqueous solutions impossible a new method of calculation was worked out. This method has been programmed for an electronic digital computor and gives reliable values of the constants even if experimental data are used from a smaller pH-range than in previously used graphical methods. In order to test this new method of calculation it was tried on *para*-Fluoro Malachite Green (*p*-FMG). This dye permits reliable measurements also in weakly alkaline and neutral aqueous solutions. Therefore, the experimental data of *p*-FMG have first been treated with the graphical methods reported below and accurate values of all of the constants were thus obtained. Then a limited amount of data, corresponding to the experimental data obtainable for *p*-BrMG and *p*-IMG, were treated with the electronic computor and the values that were obtained, were close to those calculated graphically, but the error limits for some of the constants were greater.
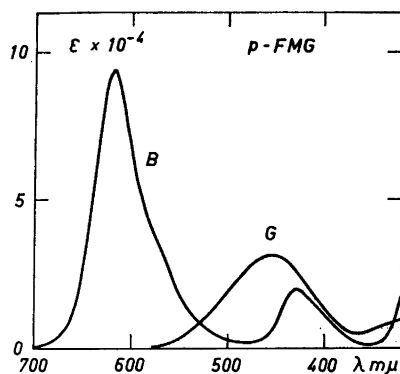
Fig. 1. Absorption curves of *p*-FMG. B is the curve of the blue-green ion $[(Me_2NC_6H_4)_2CC_6H_4F]^+$ in acetate buffer. G is the curve of the yellow ion $\left[\begin{array}{c}Me_2NC_6H_4 \\ Me_2HNC_6H_4\end{array} \!\!> CC_6H_4F\right]^{2+}$ in dilute hydrochloric acid.

EXPERIMENTAL

Chemicals and solutions. The leuco bases of the dyes were prepared in a nitrogen atmosphere by refluxing for 18 h the *p*-halide benzaldehyde (from L. Light, Colnbrock, Great Britain) (0.05 mole), N,N-dimethylaniline (0.15 mole), conc. hydrochloric acid (0.15 mole), and urea (0.05 mole). The leuco bases were recrystallized from benzene-ethanol. White needles, m.p. 104°C (*p*-fluoro leuco MG), 121°C (*p*-bromo leuco MG) and 139°C (*p*-iodo leuco MG) were obtained.

The dyestuffs were prepared by oxidizing 0.01 mole of the leuco bases dissolved in 5 ml of 5 M hydrochloric acid and diluted with 500 ml of 10 % acetic acid. For an oxidizing agent 0.01 mole of lead dioxide was used. From the oxidized products the perchlorates were prepared and they were obtained as green crystals with a metallic lustre. *p*-Fluoro Malachite Green perchlorate: (Found: C 61.9; H 5.40; N 6.32; Cl 7.62; F 4.21. Calc. for $C_{23}H_{24}O_4N_2ClF$: C 61.8; H 5.41; N 6.27; Cl 7.94; F 4.25). *p*-Bromo Malachite Green perchlorate: (Found: C 54.7; H 4.78; N 5.48. Calc. for $C_{23}H_{24}O_4N_2ClBr$: C 54.4; H 4.76; N 5.52). *p*-Iodo Malachite Green perchlorate: (Found: C 50.5; H 4.37; O 11.51; N 4.76; Cl 6.31; I 22.9. Calc. for $C_{23}H_{24}O_4N_2ClI$: C 49.8; H 4.36; O 11.54; N 5.05; Cl 6.39; I 22.9).

Stock solutions of the dyes were prepared in the same manner as before.[2] The chemicals used for the buffer solutions and the apparatus used for the measurements were the same as in Ref.[2]

MEASUREMENTS AND RESULTS

The absorption curves of *p*-FMG, *p*-BrMG and *p*-IMG are very similar to and of the same general shape as most of the derivatives of Malachite Green. Fig. 1 shows the absorption curves of *p*-FMG and Table 1 gives some values from the absorption curves of the three dyes now investigated.

Determination of K_1. The constant K_1 is determined from measurements in HCl + KCl-buffers. It was found that the absorption of the species G

Table 1. Some values from the absorption curves of *p*-FMG, *p*-BrMG and *p*-IMG.

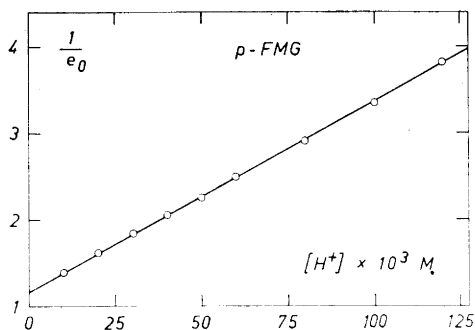|	$\lambda_{B \text{ max}}$ mμ	$\varepsilon_{B \text{ max}} \times 10^{-4}$	$\lambda_{G \text{ max}}$ mμ	$\varepsilon_{G \text{ max}} \times 10^{-4}$
p-Fluoro MG	618 and 428	9.40 and 1.95	455	3.12
p-Bromo MG	625 and 430	9.15 and 2.20	458	3.43
p-Iodo MG	625 and 435	8.85 and 2.32	458	3.50

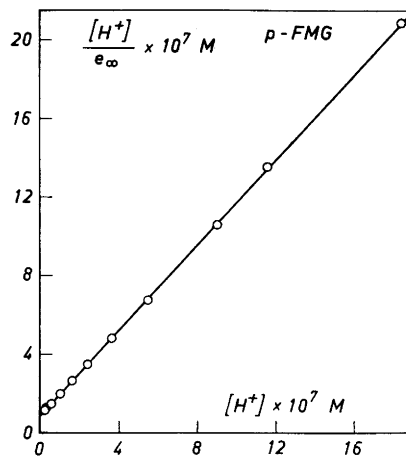*Fig. 2.* p-FMG. $1/e_0$ plotted against [H+] for the determination of K_1.

Fig. 3. p-FMG. [H+]/e_∞ plotted against [H+] for the determination of K_4/K_6.

can be neglected at the wavelengths where the species B have their principal absorption maxima, and since the measurements were carried out at these wavelengths eqn. (1) was approximated and written

$$1/e_0 = hK_1/e_B + 1/e_B \tag{4}$$

Fig. 2 shows $1/e_0$ as a function of [H+] for p-FMG. The following values were obtained:

p-Fluoro MG: $K_1 = 18.6 \pm 0.3$ M
p-Bromo MG: $K_1 = 18.2 \pm 0.2$ M
p-Iodo MG: $K_1 = 18.5 \pm 0.4$ M

Determination of K_4/K_6. It was possible to obtain reliable equilibrium absorbancies in phosphate buffers, pH 5.7—7.8, only for p-FMG. Eqn. (2) was approximated and written

$$\frac{h}{e_\infty} = \frac{1}{e_B K_6/K_4} + \frac{h(1 + 1/K_6)}{e_B} \tag{5}$$

In Fig. 3 we can see [H+]/e_∞ as a function of [H+]. From the graph we obtain (since $e_B = 0.937$) $K_4/K_6 = (8.3 \pm 0.2) \times 10^{-8}$ M.

Determination of K_2. The constant K_2 was determined from equilibrium measurements in HCl + KCl-buffers. The experimentally obtained e_∞-values are recorded in Table 2 and the following K_2-values were obtained:

p-Fluoro MG: $K_2 = 21.5 \pm 0.6$
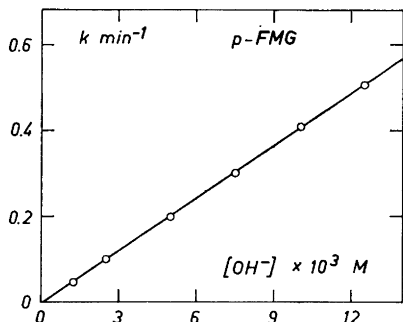p-Bromo MG: $K_2 = 35.8 \pm 0.4$
p-Iodo MG: $K_2 = 30.0 \pm 0.7$

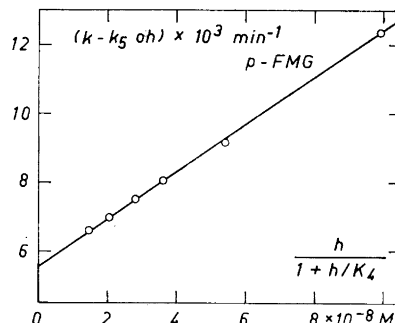*Fig. 4.* *p*-FMG. The rate constant *k* as a function of [OH⁻] for the determination of k_5.

Fig. 5. *p*-FMG. $k - k_5[OH^-]$ plotted against $[H^+]/(1 + [H^+]/K_4)$ for the determination of k_3 and K_4/K_6.

Determination of k_5. It was possible to measure the fading rate in strong alkaline solutions for all three dyes, if the concentrations of the dyestuffs were kept as low as 5×10^{-6} M, since the carbinols do not precipitate instantaneously when the solutions are saturated with the carbinols. In the used concentration range of hydroxide, [OH⁻] = 0.001−0.013 M, eqn. (3) can be approximated to

$$k = k_5 \times oh \tag{6}$$

In Fig. 4 the rate constant k is plotted against [OH⁻] for *p*-FMG. The following results were obtained.

p-Fluoro MG: $k_5 = 40.5 \pm 0.5$ min⁻¹ M⁻¹
p-Bromo MG: $k_5 = 44.3 \pm 0.5$ min⁻¹ M⁻¹
p-Iodo MG: $k_5 = 43.6 \pm 0.4$ min⁻¹ M⁻¹

Determination of k_3. Only *p*-FMG permitted reliable measurements in phosphate buffers, pH 5.7−7.8. In this pH-range eqn. (3) can be approximated and written as

$$k - k_5 oh = k_3 + k_3 \cdot \frac{K_6}{K_4} \frac{h}{1 + h/K_4} \tag{7}$$

In Fig. 5 $k - k_5 oh$ is plotted against $h/(1 + h/K_4)$. Since h/K_4 is considerably less than 1 in the actual pH-range, it is sufficient to use, as a first approximation, an approximate value of K_4. From Fig. 5 we obtain for *p*-Fluoro MG: $k_3 = (5.58 \pm 0.06) \times 10^{-3}$ min⁻¹ and $K_4/K_6 = (8.2 \pm 0.2) \times 10^{-8}$ M. The value of K_4/K_6 is in good agreement with the value 8.3×10^{-8} that was obtained from the equilibrium measurements.

Determination of k_1 and k_2. The rate constants k_1 and k_2 were obtained from measurements of the fading rates in HCl + KCl-buffers. They were calculated from eqn. (3).

p-Fluoro MG: $k_1 = 0.154 \pm 0.02$ min⁻¹; $k_2 = (72 \pm 2) \times 10^{-4}$ min⁻¹
p-Bromo MG: $k_1 = 0.140 \pm 0.01$ min⁻¹; $k_2 = (39.2 \pm 0.8) \times 10^{-4}$ min⁻¹
p-Iodo MG: $k_1 = 0.137 \pm 0.04$ min⁻¹; $k_2 = (45 \pm 2) \times 10^{-4}$ min⁻¹

Table 2. Obtained values of e_0, e_∞ and k for the determination of K_1, K_2, k_1 and k_2.
$C_M = 1 \times 10^{-5}$ M, $d = 1-5$ cm, $T = 20.0°C$.

[H⁺]M	p-FMG. $e_B = 0.940$			p-BrMG. $e_B = 0.911$			p-IMG. $e_B = 0.884$		
$[H^+]M$	e_0	$e_\infty \times 10^2$	$k \times 10^2$ min⁻¹	e_0	$e_\infty \times 10^2$	$k \times 10^2$ min⁻¹	e_0	$e_\infty \times 10^2$	$k \times 10^2$ min⁻¹
0.010	0.736	1.20	3.75	0.710	1.16	3.14	0.683	1.12	3.18
0.020	0.716	1.44	5.36	0.614	1.40	4.64	0.588	1.34	4.61
0.030	0.677	1.90	6.56	0.555	1.70	5.81	0.522	1.66	5.77
0.040	0.639	2.26	7.54	0.496	2.24	6.71	0.485	2.22	6.65
0.050	0.603	2.74	8.35	0.451	2.64	7.45	0.438	2.60	7.45
0.060	0.564	3.60	9.08	0.401	3.26	8.04	0.398	3.20	7.91
0.080	0.503	4.28	10.19	0.341	4.28	9.00	0.339	4.28	8.86
0.100	0.441	5.30	11.08	0.305	6.24	9.58	0.287	6.24	9.55
0.120	0.385	6.86	11.76	0.270	11.56	10.10	0.253	11.36	9.90

Determination of the remaining constants K_3, K_4, K_6, k_3, k_4 *and* k_6. The values of these constants were determined by kinetic measurements in acetate buffers, pH = 3.3—5.3. (p-BrMG and p-IMG) and acetate buffers and phosphate buffers, pH = 3.5—7.9 (p-FMG). They were calculated from eqn. (3). The following results were obtained:
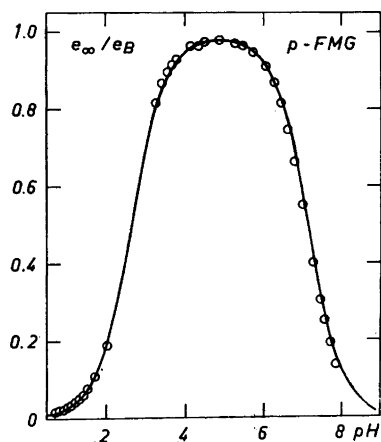

Fig. 6. p-FMG. The equilibrium absorbancy, given as the fraction of the specific absorbancy of B, e_∞/e_B, as a function of pH. The symbols O are experimental values. The full drawn curve is calculated from eqn. (2).
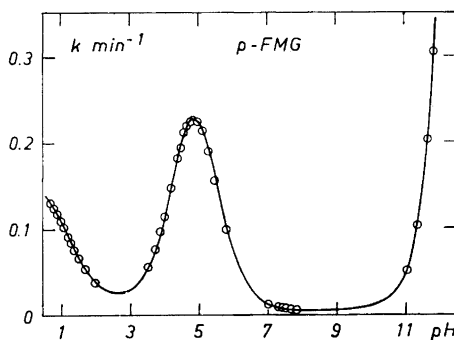
Fig. 7. p-FMG. The rate constant of the over-all reaction k as a function of pH. The symbols O are experimental values. The full drawn curve is calculated from eqn. (3).
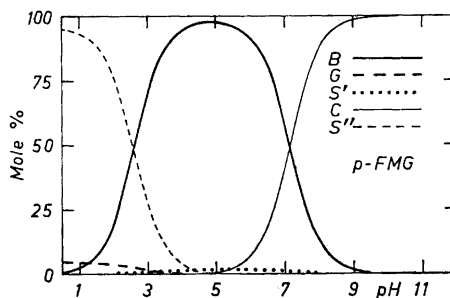
Fig. 8. *p*-FMG. The distribution of the dye between the different species as a function of pH at equilibrium.

p-Fluoro MG: $K_3 K_4 = (1.76 \pm 0.06) \times 10^{-10}$ M^2; $K_3 = (3.6 \pm 0.1) \times 10^{-5}$ M; $K_4 = (4.9 \pm 0.2) \times 10^{-6}$ M; $K_6 = 69 \pm 2$; $k_4 = 0.38 \pm 0.01$ min^{-1}; $k_6 = (7.1 \pm 0.3) \times 10^{-6}$ min^{-1}

p-Bromo MG: $K_3 = (3.8 \pm 0.2) \times 10^{-5}$ M; $K_4 = (6.1 \pm 0.4) \times 10^{-6}$ M; $K_6 = 40 \pm 2$; $k_3 = (5.8 \pm 0.1) \times 10^{-3}$ min^{-1}; $k_4 = 0.234 \pm 0.006$ min^{-1}; $k_6 = (3.6 \pm 0.4) \times 10^{-6}$ min^{-1}

p-Iodo MG: $K_3 = (3.6 \pm 0.3) \times 10^{-5}$ M; $K_4 = (6.3 \pm 1.1) \times 10^{-6}$ M; $K_6 = 49 \pm 4$; $k_3 = (4.9 \pm 0.1) \times 10^{-3}$ min^{-1}; $k_4 = 0.24 \pm 0.01$ min^{-1}; $k_6 = (4.3 \pm 1.1) \times 10^{-6}$ min^{-1}

Some results of the measurements of *p*-FMG are collected in Figs. 6 and 7. Fig. 6 shows the equilibrium absorbancy as a function of pH. The full drawn curve is calculated from eqn. (2) with the values of the constants given above. The

Table 3. Corresponding values of the constants for a comparison between Malachite Green and its *para*-halide derivatives.

Dyestuff	$1/K_1$ (M)	$K_3 \times 10^5$ (M)	$K_4 \times 10^6$ (M)	K_2	$1/K_6$
Malachite Green[a]	0.036	2.7	5.8	22	0.0147
p-Fluoro MG	0.054	3.6	4.85	21.5	0.0145
p-Chloro MG[a]	0.052	6.3	5.2	25	0.0303
p-Bromo MG	0.055	3.8	6.1	35.8	0.0250
p-Iodo MG	0.054	3.6	6.3	30.0	0.0204

Dyestuff	$k_1 \times 10^2$ (min^{-1})	$k_2 \times 10^2$ (min^{-1})	$k_3 \times 10^2$ (min^{-1})	k_4 (min^{-1})	k_5 (M^{-1}min^{-1})	$k_6 \times 10^6$ (min^{-1})
Malachite Green[a]	16.8	0.78	0.65	0.44	31.7	4.6
p-Fluoro MG	15.4	0.72	0.55	0.38	40.5	7.1
p-Chloro MG[a]	14.5	0.58	0.60	0.20	44.2	3.5
p-Bromo MG	14.0	0.39	0.58	0.23	44.3	3.6
p-Iodo MG	13.7	0.45	0.49	0.24	43.6	4.3

a) The values of K_1, K_2, K_3, K_4, K_6, k_1, k_2, k_3, and k_4 are from Ref.[3] whereas k_5 and k_6 have been determined now.

symbols O are experimental values. Fig. 7 shows the rate constant of the over-all reaction as a function of pH. The full drawn curve is calculated from eqn. (3) with the values of the constants given above and the symbols are experimental values.

The distribution of the five species of p-FMG as a function pH is shown in Fig. 8. Since *para*-fluoro Malachite Green is very similar to the parent dye Malachite Green, a distribution diagram of Malachite Green would be almost similar to Fig. 8.

DISCUSSION

A comparison between all the *para*-halide derivatives of Malachite Green and Malachite Green can be made with the aid of Table 3. As a general remark it can be said that the *para*-halide substituents have a comparatively small influence on the protolytic and hydration equilibria and the reaction rates. The *para*-bromo and *para*-iodo derivatives are extremely similar in their behaviour and quite different from corresponding *ortho*-derivatives (Ref.[1]). This proves that the position of large substituents, like the bromo- and iodo-substituents, is of greater importance for the behaviour of the Malachite Green dyes than the nature of the substituents.

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3. Cigén, R. *Protolysengleichgewichte und Reaktionsgeschwindigkeiten einiger basischer Tri-phenylmethanfarbstoffe* (Diss.), University, Lund 1956.