

Equilibrium and Kinetic Studies on Halide Derivatives of Malachite Green

IV. *m*-Chloro, *m*-Bromo, and *m*-Iodo Malachite Green

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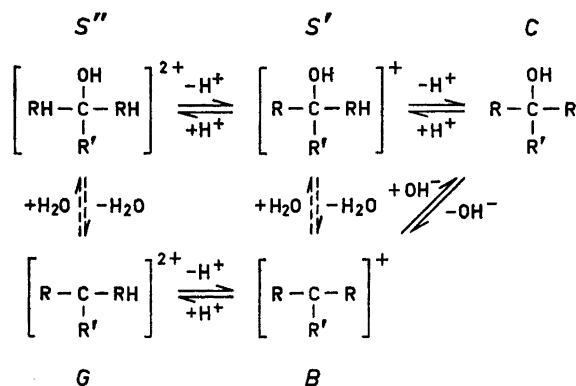
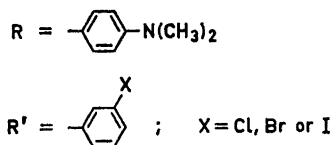
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The series of investigations of protolytic and hydration equilibria and reaction rates of basic triphenylmethane dyes is continued with the investigations of *m*-Chloro, *m*-Bromo, and *m*-Iodo Malachite Green. Three protolytic, two hydration, and 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 the *para*-halide derivatives shows that there is no marked differences between the two sets of dyes as regards the protolytic reactions, whereas the hydration reactions are facilitated when the substituent is in the *meta*-position. This influence, however, is by no means so great as that caused by the substituents in the *ortho*-position.

The *meta*-halide derivatives have even less soluble carbinols than the corresponding *ortho*- and *para*-derivatives, and like those, the solubility decreases with the increasing atom weight of the halide substituent. Because of the minor solubility the upper pH-limit for reliable measurements lies somewhere between 5 and 6, depending on dyestuff and concentration. Nevertheless, it has been possible to perform reliable kinetic measurements in strongly alkaline solutions, where the fading rates are great, since the carbinols do not precipitate instantaneously when the solutions are saturated with the carbinols.

Neutral aqueous solutions of the dyestuffs now investigated are blue-green. In strongly acid solutions they turn yellow at first and are then strongly decoloured. In alkaline solutions they are colourless. The reactions may be written schematically in the following way, where



Definitions of constants and symbols are the same as in Ref.⁷

EQUATIONS

The following expressions for e_0 , e_∞ , and k can be derived:^{1,3}

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

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

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

The term $K_1 h e_G$ 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

Chemicals and solutions. *m*-Chloro Malachite Green. The leuco compound was prepared in a nitrogen atmosphere, through condensation of *m*-chlorobenzaldehyde with *N,N*-dimethylaniline in conc. hydrochloric acid and urea. The leuco compound was recrystallized from benzene-ethanol. White crystals, m.p. 114°C, were obtained. The dyestuff was prepared by oxidizing, with lead dioxide, and the leuco compound dissolved in a calculated amount of 5 M hydrochloric acid, and diluted with 10 % acetic acid. From the oxidized product a perchlorate was prepared that was obtained as small green crystals after repeated recrystallization from diluted acetic acid. (Found: C 59.4; H 5.3; O 13.6; N 5.9; Cl 15.5. Calc. for $\text{C}_{23}\text{H}_{24}\text{O}_4\text{N}_2\text{Cl}_2$: C 59.61; H 5.22; O 13.81; N 6.05; Cl 15.31.)

Table 2. Obtained values of e_0 , e_∞ , and k in HCl—KCl buffers.

[H ⁺] M	<i>m</i> -Cl MG			<i>m</i> -Br MG			<i>m</i> -I MG		
	e_0	e_∞	$k \times 10^2$ min ⁻¹	e_0	e_∞	$k \times 10^2$ min ⁻¹	e_0	e_∞	$k \times 10^2$ min ⁻¹
2×10^{-5}		0.852			0.790			0.410	
0.01	0.718	0.0723	2.91	0.659	0.0695	2.74	0.645	0.0447	2.75
2	618	377	4.40	572	363	4.15	561	235	4.13
3	544	259	5.48	514	243	5.20	500	159	5.19
4	488	191	6.58	450	187	6.21	442	128	6.11
5	444	169	7.34	412	165	6.92	410	103	6.79
6	406	133	7.82	375	129	7.45	379	083	7.24
7		113			113			075	
8	340	094	8.73	317	093	8.43	322	059	8.20
0.10	0.304	0.0077	9.37	0.282	0.0075	8.97	0.284	0.0048	8.83

Table 3. Obtained values of e_∞ in acetate buffers.

pH	e_∞		
	<i>m</i> -Cl MG	<i>m</i> -Br MG	<i>m</i> -I MG
3.23	0.575	0.537	0.557
3.52	707	657	669
3.73	762	714	714
4.01	827	757	747
4.32	852	792	782
4.59	867	802	760
4.87	867	807	787
5.11	857	792	787
5.46	837	762	750
5.78	0.767	0.707	0.694

Table 4. Obtained values of k in acetate buffers.

pH	k min ⁻¹		
	<i>m</i> -Cl MG	<i>m</i> -Br MG	<i>m</i> -I MG
3.54	0.0252	0.0255	0.0279
3.74	321	332	362
3.89	393	404	443
4.01	476	470	549
4.09	—	539	593
4.16	—	582	655
4.23	591	595	741
4.32	—	680	749
4.41	711	713	805
4.50	752	769	872
4.59	775	778	894
4.67	801	815	930
4.77	843	837	928
4.87	805	841	918
4.98	796	812	845
5.11	734	—	—
5.25	0.0659	—	—

Table 5. Obtained values of k in NaOH—KCl buffers.

[OH ⁻] M	$k \text{ min}^{-1}$		
	<i>m</i> -Cl MG	<i>m</i> -Br MG	<i>m</i> -I MG
0.0020	0.0834	0.0822	0.0748
40	1727	1849	1672
48	2119	2004	1981
60	282	270	255
72	332	328	301
80	361	346	331
96	449	448	415
100	469	453	425
0.0120	0.553	0.527	0.521

Table 6. Constants and variables of the polynomials used in the calculation.

Polynomials						from eqn.	buffer system
No.	variables		constants				
	y	x	a_0	a_1	a_2		
PI	$\frac{1}{e_0}$	h	$\frac{1}{e_{B'}}$	$\frac{K_1}{e_{B'}}$	—	1	HCl—KCl
PII	$\frac{e_B}{e_\infty} \cdot h^a$	h	K_4/K_6	$1 + 1/K_6$	$K_1(1+K_2)$	2	HCl—KCl acetate phosphate
PIIIa	$\frac{k}{1 + K_1h + \frac{1}{K_1K_2h + 1/K_6}}$	h	k_3	k_1K_1	—	3	HCl—KCl
PIIIb	$\frac{h}{k'}$	h	$\frac{K_4}{k_4}$	$\frac{1}{k_4}$	$\frac{1}{k_4K_3}$	3	acetate
PIIIc	$k - k_5oh$	$\frac{h}{1 + \frac{h}{K_4}}$	k_3	$\frac{k_4}{K_4}$	—	3	phosphate
PIIIId	k	oh	k_3	k_5	—	3	NaOH—KCl

$$a \ e_B = e_{B'}(1 + K_1(1 + K_2) \cdot h' + 1/K_6(1 + K_4/h')).$$

$$b \ k' = k - \frac{k_1K_1h + k_3}{1 + K_1h} - \frac{k_2h^2}{h^2 + K_3h + K_3K_4}$$

Measurements of e_0 , e_∞ , and k in HCl—KCl buffers (Table 2), e_∞ and k in acetate buffers (Tables 3 and 4), and k in NaOH—KCl buffers (Table 5) have been performed as in Ref.⁴

For the calculation the eqns. (1), (2), and (3) have been transformed and approximated in various ways to polynomials of the first or the second degree, *i.e.* $y = \sum_{k=0}^n a_k x^k$; $n = 1$ or 2 (Table 6). The constants in these polynomials and their standard deviations have been calculated with the aid of the least square

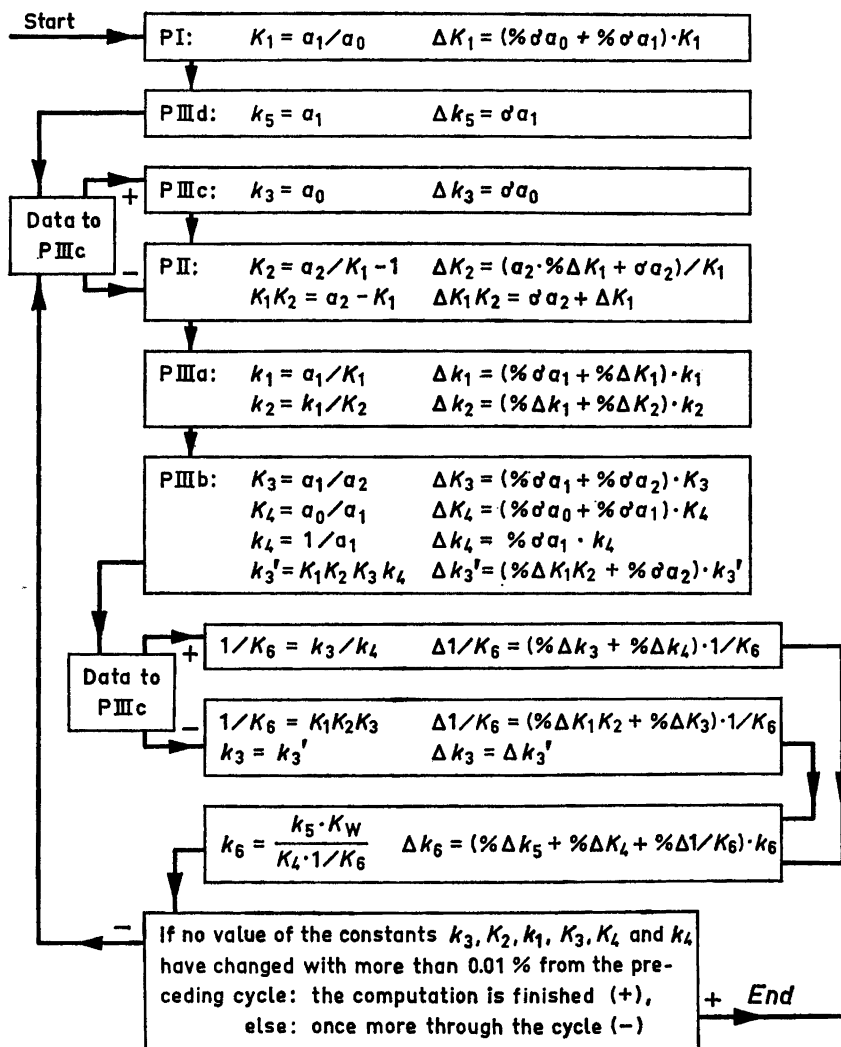


Fig. 2. Block scheme of the computation. ΔK_i = the error limit in K_i ; $\% \Delta K_i = (\Delta K_i)/K_i$; σa_i = the standard deviation in the polynomial constant a_i ; $\% \sigma a_i = (\sigma a_i)/a_i$. For the meaning of the various a_0 , a_1 , and a_2 see Table 6. The block "data to PIIIc" means: if measurements have been performed in phosphate buffers, the computation goes the way marked "+", else "-".

method,⁵ taking the weights in the error square sum inverse proportional to the squares of the corresponding ordinate values, *i.e.* $w_i = \text{const. } y_i^{-2}$. Finally, the sought constants and their error limits have been calculated from the polynomial constants and their standard deviations. The computation, coded for a highspeed electronic computer (SMIL), has been constructed as an iteration process with null as initial value of the correction terms. A schematic summary of the computation is given in Fig. 2. The results obtained are tabulated in Table 7.

Table 7. Obtained values of the constants and their error limits.

	K_1 M ⁻¹	K_2	$K_3 \times 10^5$ M	$K_4 \times 10^6$ M	$1/K_5$
<i>m</i> -Cl MG	17.8 ± 0.5	64 ± 3	3.9 ± 0.2	6.4 ± 0.4	0.046 ± 0.002
<i>m</i> -Br MG	17.8 ± 0.5	61 ± 2	4.2 ± 0.3	5.8 ± 0.9	0.046 ± 0.004
<i>m</i> -I MG	16.2 ± 0.4	52 ± 2	3.5 ± 0.3	10.2 ± 1.6	0.029 ± 0.003

	$k_1 \times 10^3$ min ⁻¹	$k_2 \times 10^3$ min ⁻¹	$k_3 \times 10^3$ min ⁻¹	$k_4 \times 10^3$ min ⁻¹	k_5 min ⁻¹ M ⁻¹	$k_6 \times 10^6$ min ⁻¹
<i>m</i> -Cl MG	142 ± 5	2.2 ± 0.2	6.1 ± 0.1	137 ± 4	48.2 ± 0.6	2.1 ± 0.3
<i>m</i> -Br MG	135 ± 5	2.2 ± 0.2	6.1 ± 0.2	135 ± 6	46.6 ± 0.6	2.2 ± 0.6
<i>m</i> -I MG	136 ± 4	2.6 ± 0.2	5.3 ± 0.2	180 ± 12	44.6 ± 0.5	1.9 ± 0.5

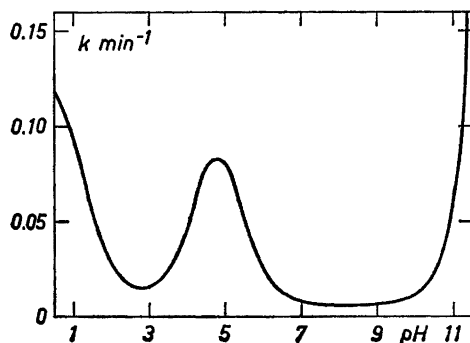


Fig. 3. *m*-Bromo MG. The rate constant of the over-all reaction, k , as a function of pH.

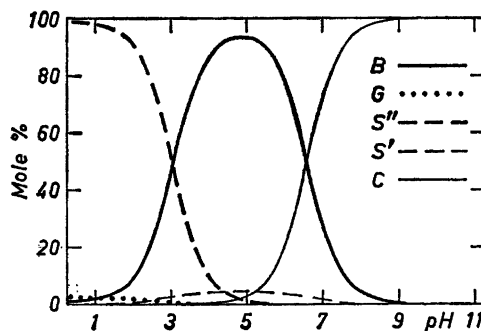


Fig. 4. *m*-Bromo MG. The distribution of the dye between the different species as a function of pH at equilibrium.

Fig. 3 shows the rate constant of the over-all reaction and Fig. 4 the distribution of the five species of *m*-Bromo MG as functions of pH.

DISCUSSION

In previous investigations it has been demonstrated that bulky substituents in the *ortho*-position cause a strong steric hindrance to the hydration reac-

Table 8. Corresponding values of the constants for a comparison between Malachite Green and its mono-bromo derivatives.

	K_2	K_6	$\frac{K_1}{M^{-1}}$	$K_3 \times 10^5$ M	$K_4 \times 10^6$ M
MG	22	68	28	2.7	5.8
<i>o</i> -Br MG	1.05	1550	17.4	3.5	5.6
<i>m</i> -Br MG	61	22	17.8	4.2	5.8
<i>p</i> -Br MG	36	40	18.2	3.8	6.1

	$k_1 \times 10^2$ min ⁻¹	$k_2 \times 10^2$ min ⁻¹	$k_3 \times 10^2$ min ⁻¹	$k_4 \times 10^2$ min ⁻¹	k_5 min ⁻¹ M ⁻¹	$k_6 \times 10^6$ min ⁻¹
MG	16.8	0.78	0.65	43.9	31.7	4.6
<i>o</i> -Br MG	0.13	0.12	0.0064	9.9	1.08	3.7
<i>m</i> -Br MG	13.5	0.22	0.61	13.5	46.6	2.2
<i>p</i> -Br MG	14.0	0.39	0.58	23.4	44.3	3.6

tions,^{1,2,6,7} whereas substituents in the *para*-position have only a small influence on the reactions.^{1,8} The *meta*-halide derivatives now investigated are among themselves very similar in their behaviour, and on the whole they also resemble the *para*-halide derivatives and the unsubstituted Malachite Green. There is a certain difference in regard to the hydration reactions, however. These reactions are somewhat facilitated when there is a substituent in the *meta*-position. Thus the values of the hydration constants K_2 and $1/K_6$ of the *meta*-halide derivatives are about three times as great as the values of the corresponding constants of Malachite Green. As a representative selection the values of the constants of Malachite Green and its three mono-Bromo derivatives are shown together in Table 8.

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