

Equilibrium and Kinetic Studies on Halide Derivatives of Malachite Green

II. *o*-Bromo and *o*-Iodo Malachite Green

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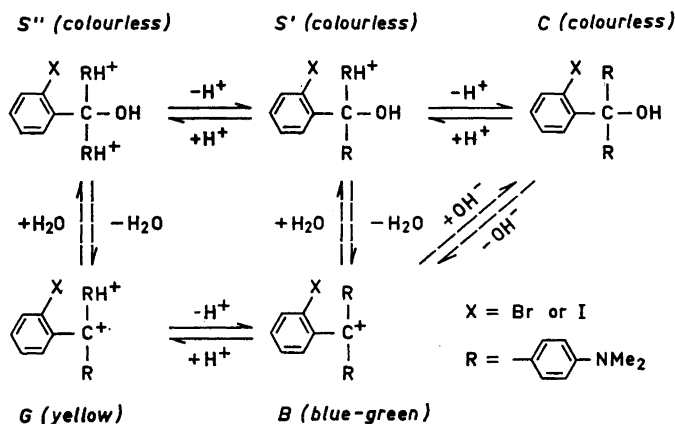
The series of investigations of protolytic and hydration equilibria and reaction rates of basic triphenylmethane dyes is continued with the investigations of *o*-Bromo and *o*-Iodo Malachite Green.

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 (MG) and *o*-Fluoro MG shows that the bulky bromo- and iodo-substituents in the *ortho* position cause a very strong "steric hindrance" of the hydration reactions. Thus the hydration constant $K_{2(\text{MG})} = 22$, whereas $K_{2(o-\text{BrMG})} = 1.05$ and $K_{2(o-\text{IMG})} = 0.27$ and the rate constant $k_{1(\text{MG})} = 0.17$, whereas $k_{1(o-\text{BrMG})} = 0.0013$ and $k_{1(o-\text{IMG})} = 0.00036 \text{ min}^{-1}$.

Preliminary investigations of *o*-Bromo and *o*-Iodo Malachite Green indicated some very striking differences between these dyes and *o*-Fluoro Malachite Green (*o*-FMG) and the parent dye Malachite Green (MG). Thus *o*-Bromo MG (*o*-BrMG) and *o*-Iodo MG (*o*-IMG) are considerably more alkali-resistant than MG, *i.e.* they are decolourized at a higher pH and more slowly than MG. *o*-BrMG and *o*-IMG are also partially decolourized in acid solutions, pH 0–2, but not to such a high degree and not so fast as MG.

The protolytic and hydration reactions of *o*-BrMG and *o*-IMG can be visualized by the following reaction scheme.

The above-mentioned differences between MG and its *o*-bromo and *o*-iodo derivatives indicate that the bulky bromo- and iodo-substituents in the *ortho* position cause a very strong "steric hindrance" of the hydration reactions $\text{B} + \text{H}_2\text{O} \longrightarrow \text{S}'$ and $\text{G} + \text{H}_2\text{O} \longrightarrow \text{S}''$. An attempt to determine the protolytic, hydration, and rate constant of *o*-BrMG and *o*-IMG with the same methods as those used in our previous investigations of similar dyes¹⁻⁵ was



not very successful, since the hydration reactions proceed very slowly at $\text{pH} = 9-10$ — "halftimes" of a few weeks — and the solubility of the carbinols, C , is very low, about 10^{-7} M. Furthermore, the equilibrium $B + \text{H}_2\text{O} \rightleftharpoons S'$ is so strongly displaced towards the coloured species B that within the pH -range 3—7 the dyes at equilibrium are almost completely dehydrated. However, with the aid of a partially new experimental technique and a new way of treating the results of the measurements we have succeeded in determining the constants listed below.

Definitions of constants and symbols:

$$K_1 = [\text{G}]/[\text{B}][\text{H}^+]; K_2 = [\text{S}'']_{\infty}/[\text{G}]_{\infty}; K_3 = [\text{S}'][\text{H}^+]/[\text{S}'];$$

$$K_4 = [\text{C}][\text{H}^+]/[\text{S}']; K_6 = [\text{B}]_{\infty}/[\text{S}']_{\infty}$$

$$h = [\text{H}^+]; \text{oh} = [\text{OH}^-]; K_w = [\text{H}^+][\text{OH}^-].$$

k_1	=	rate constant for the reaction	$\text{G} + \text{H}_2\text{O} \rightarrow \text{S}''$
k_2	=	»	»
k_3	=	»	»
k_4	=	»	»
k_5	=	»	»
k_6	=	»	»
k	=	»	»

ϵ_B, ϵ_G = the molar extinction coefficient of B and G .

e_0, e_t, e_{∞} = the absorbancy per cm of a solution at the times 0 and t and at equilibrium.

E_0, E_t, E_{∞} = the total absorbancy.

e_B, e_G = the absorbancy per cm of a solution containing only B or G .

C_M = the total concentration of dyestuff.

The constants in the equilibrium scheme can be calculated, if the following quantities are determined for a large number of solutions with different pH -values:

- (1) The absorbancy, e_0 , at a moment immediately after the mixing of a dye stock solution with the appropriate buffers. The dye stock solution is (if

possible) prepared in such a way that all of the dye is present as the coloured species B.

- (2) The absorbancy, e_{∞} , when equilibrium is reached.
- (3) The over-all rate constant, k , for the reactions that change the intensity of the colour of the solutions either by the hydration of the coloured species (B and G) to colourless species (C, S', S'') or *vice versa*.
- (4) The pH of the solutions.

EQUATIONS

The following expressions for the initial absorbancy, e_0 , the equilibrium absorbancy, e_{∞} , and the rate constant of the over-all reaction, k , as functions of the hydrogen ion concentration, can be derived:

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

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

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

The eqns. (1–3) can be approximated, since certain species and reaction steps can be neglected in some pH-ranges. These approximations and the transformations of the equations will be further considered in connection with the determination of the individual constants.

EXPERIMENTAL

Preparation of the dyestuffs. *o*-Iodo Malachite Green. The leuco base was prepared in a nitrogen atmosphere by refluxing for 18 h *o*-iodobenzaldehyde (0.05 mole), N,N-dimethylaniline (0.15 mole), conc. hydrochloric acid (0.15 mole), and urea (0.05 mole). The leuco base was recrystallized from benzene-ethanol. White needles, m.p. 143°C, were obtained. 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 an oxidizing agent 0.01 mole of lead dioxide was used. From the oxidized product the perchlorate was prepared, and it was obtained as small green crystals. (Found: C 50.8; H 4.39; N 5.15; O 11.40, Cl 6.02; I 22.64. Calc. for C₂₃H₂₄O₄N₂ClI: C 49.8; H 4.36; N 5.05; O 11.54; Cl 6.39; I 22.87).

o-Bromo Malachite Green was prepared in the same manner as *o*-IMG. The leuco base was obtained as white needles, m.p. 149°C, and the perchlorate of the dyestuff as very well crystallized bronze coloured needles.

Stock solutions of the dyes were prepared in the same manner as in Ref.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 *o*-BrMG and *o*-IMG are very similar and, therefore, only the absorption curves of *o*-BrMG have been drawn in Fig. 1.

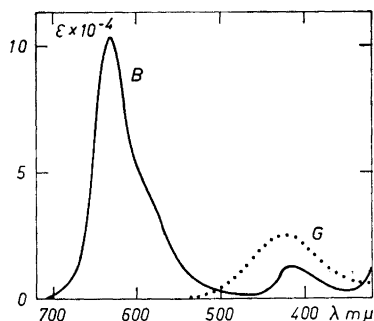
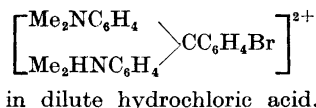


Fig. 1. *o*-BrMG. Absorption curves. B is the curve for the blue-green ion $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{Br}]^+$ in acetate buffer, G is the curve for the yellow ion



The following values were obtained:

o-Bromo MG

$$\lambda_{\text{B max}} = 631 \text{ m}\mu \text{ resp. } 414 \text{ m}\mu$$

$$\epsilon_{\text{B max}} = 10.3 \times 10^4 \text{ resp. } 1.25 \times 10^4$$

$$\lambda_{\text{G max}} = 422 \text{ m}\mu$$

$$\epsilon_{\text{G max}} = 2.50 \times 10^4$$

o-Iodo MG

$$\lambda_{\text{B max}} = 629 \text{ m}\mu \text{ resp. } 416 \text{ m}\mu$$

$$\epsilon_{\text{B max}} = 9.7 \times 10^4 \text{ resp. } 1.15 \times 10^4$$

$$\lambda_{\text{G max}} = 423 \text{ m}\mu$$

$$\epsilon_{\text{G max}} = 1.95 \times 10^4$$

Determination of K_1 . It was found that the absorption of the species G can be neglected at the wavelengths $\lambda \approx 630 \text{ m}\mu$, where the species B have their principal absorption maxima. Therefore, eqn. (1) can be approximated and written ($e_{\text{G}} \approx 0$)

$$1/e_0 = hK_1/e_{\text{B}} + 1/e_{\text{B}} \quad (4)$$

since the measurements were carried out at the wavelengths, 629 and 631 $\text{m}\mu$. Fig. 2 shows $1/e_0$ as a function of $[\text{H}^+]$. The slopes, l , and the intercepts, y , on the ordinate axis of the obtained straight lines give for

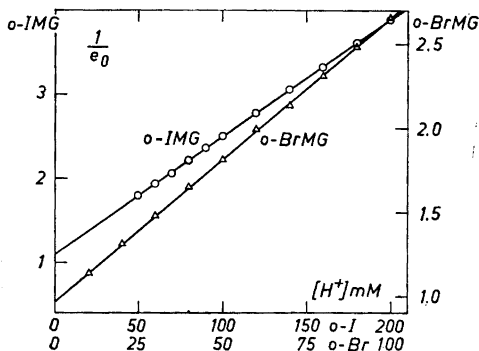


Fig. 2. *o*-BrMG and *o*-IMG. $1/e_0$ plotted vs. $[\text{H}^+]$ for the determination of K_1 .

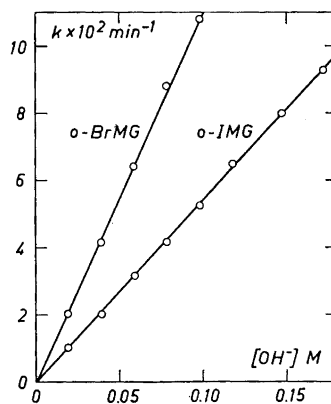


Fig. 3. *o*-BrMG and *o*-IMG. The rate constant k plotted vs. $[\text{OH}^-]$ for the determination of k_5 .

o-Bromo MG ($C_M = 1 \times 10^{-5}$ M): $l = 16.85$; $y = 0.970$; $e_B = 1.03$; $K_1 = 17.4 \pm 0.2$

o-Iodo MG ($C_M = 0.94 \times 10^{-5}$ M): $l = 14.0$; $y = 1.095$; $e_B = 0.97$;
 $K_1 = 12.8 \pm 0.2$

Determination of K_2 . Eqn. (2) was approximated and written

$$K_2 = \frac{e_B - e_\infty(1 + K_1 h)}{e_\infty K_1 h} \quad (5)$$

The equilibrium absorbancies e_∞ , were read 52 h (*o*-BrMG) and 73 h (*o*-IMG) after mixing equal volumes of a neutral dye stock solution and appropriate HCl + KCl-buffer solutions. The results of the measurements are collected in Tables 1 and 2; *o*-BrMG: $K_2 = 1.05 \pm 0.04$ *o*-IMG: $K_2 = 0.27 \pm 0.03$.

Determination of k_5 . Although the carbinol species, C, are very slightly soluble, it was possible to measure the fading rate in strongly alkaline solutions, since the carbinol does not precipitate instantaneously when the solution is saturated with the carbinol and the equilibrium absorbancy is known ($e_\infty = 0$). In Fig. 3 the rate constants, k , of the fading are plotted against $[\text{OH}^-]$ in the range $[\text{OH}^-] = 0.02\text{--}0.17$ M. In this range eqn. (3) can be approximated to

$$k = k_5 \cdot \text{oh} \quad (6)$$

and Fig. 3 gives for *o*-BrMG: $k_5 = 1.08 \pm 0.03 \text{ min}^{-1} \text{ M}^{-1}$ and for *o*-IMG: $k_5 = 0.535 \pm 0.010 \text{ min}^{-1} \text{ M}^{-1}$.

The determination of the remaining constants of the reaction scheme was somewhat troublesome, since (1) the equilibria "coloured" \rightleftharpoons "colourless" are more displaced towards the coloured species than in previously investigated dyes, (2) some of the rate constants have very low values which means, *e.g.*, that a fading reaction in the pH-range 8–10 needs 1–3 months to reach equilibrium, (3) the carbinols are very slightly soluble.

Thus it was impossible to obtain reliable rate constants of *o*-IMG from fading reactions in HCl + KCl-buffers, since the dye does not fade appreciably — *cf.* $[\text{S}'']_\infty/[\text{G}]_\infty = K_2 = 0.27$. Consequently, it was also impossible to decolorize a dye solution with dilute hydrochloric acid in order to use the decolorized solution to determine the rate at which the colour is restored, when the decolorized solution is mixed with acetate buffers, as has been done with previously investigated dyes in order to determine the constants K_3 , K_4 , K_6 and k_4 .

It should be possible to determine the rate constant k_3 from kinetic measurements in borate buffers, $\text{pH} \approx 9$. The halftime of the reaction ($\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{S}'$), however, is about a week at $\text{pH} \approx 9$ and the insoluble carbinol will precipitate before the reaction has proceeded enough to give reliable results.

The way out of these difficulties was the following. (1) A dye stock solution was decolorized and the carbinol precipitated by addition of KOH. (2) Then the alkaline solution was made acid with HCl — final $[\text{H}^+] = 0.01$ M — and from this the precipitated carbinol slowly dissolved. The reactions of this treatment of the dye stock solution are the following.

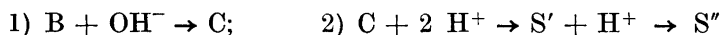


Table 1. *o*-BrMG. e_0 -, e_∞ - and k -values for the determination of K_1 , K_2 , k_1 and k_2 . $\lambda = 631$ m μ ; $T = 20.0^\circ\text{C}$; $C_M = (0.5-2) \times 10^{-5}$ M; $d = 1-2$ cm; $e_B = 1.030$; $K_1 = 17.4$.

[H ⁺] (M)	e_0	e_∞	[H ⁺] (M)	$k \times 10^3$ (min ⁻¹)
0.010	0.883	0.738	0.010	1.76
0.020	0.762	0.580	0.020	1.73
0.030	0.677	0.480	0.030	1.81
0.040	0.607	0.410	0.040	1.90
0.050	0.552	0.357	0.050	1.95
0.060	0.503	0.317	0.060	1.96
0.070	0.469	0.285	0.075	1.99
0.080	0.433	0.260	0.085	2.06
0.090	0.403	0.237	0.095	2.06
0.100	0.377	0.220		

Since the reaction $S'' \rightarrow G + H_2O$ proceeds rather slowly, the acid solution obtained from the treatment of the carbinol solution with HCl can be used as an almost decolourized dye solution in a series of kinetic measurements, where the rates of the reactions $S'' \rightleftharpoons G + H_2O$ and $S' \rightleftharpoons B + H_2O$ were determined.

Determination of k_1 and k_2 . Decolourized acid dye solutions were mixed with suitable HCl + KCl-buffers and the restoring of the colour was followed spectrophotometrically. The results are collected in Tables 1 and 2. To begin with, approximate values of k_1 and k_2 were calculated from eqn. (3) approximated as

$$k = k_2 + k_1 K_1 h / (1 + K_1 h) \quad (7)$$

Refined values were calculated later from the non-approximated eqn. (3).

o-Bromo MG: $k_1 = (1.29 \pm 0.05) \times 10^{-3}$ min⁻¹; $k_2 = (1.23 \pm 0.05) \times 10^{-3}$ min⁻¹

o-Iodo MG: $k_1 = (0.36 \pm 0.02) \times 10^{-3}$ min⁻¹; $k_2 = (1.32 \pm 0.09) \times 10^{-3}$ min⁻¹

Table 2. *o*-IMG. e_0 -, e_∞ - and k -values for the determination of K_1 , K_2 , k_1 and k_2 . $\lambda = 629$ m μ ; $T = 20.0^\circ\text{C}$; $C_M = (1-2) \times 10^{-5}$ M; $d = 1-2$ cm; $e_B = 0.900$; $K_1 = 12.8$.

[H ⁺] (M)	e_0	e_∞	[H ⁺] (M)	$k \times 10^3$ (min ⁻¹)
0.050	0.557	0.480		
0.060	0.517	0.442		
0.070	0.487	0.410	0.0746	1.66
0.080	0.452	0.380	0.0846	1.65
0.090	0.424	0.354	0.0946	1.65
0.100	0.401	0.332	0.1046	1.64
0.120	0.361	0.296	0.1246	1.64
0.140	0.328	0.268	0.1446	1.64
0.160	0.301	0.244	0.1646	1.64
0.180	0.277	0.224	0.1846	1.64
0.200	0.257	0.208	0.2046	1.64

Table 3. *o*-BrMG. Kinetic measurements in acetate buffers. $\lambda = 631 \text{ m}\mu$; $T = 20.0^\circ\text{C}$; $C_M = 5 \times 10^{-6} \text{ M}$.

pH	$k \text{ min}^{-1}$	pH	$k \text{ min}^{-1}$
4.14	0.0327	4.88	0.0550
4.24	0.0367	4.93	0.0549
4.33	0.0407	4.98	0.0545
4.42	0.0459	5.11	0.0511
4.51	0.0482	5.19	0.0492
4.60	0.0506	5.28	0.0433
4.69	0.0530	5.35	0.0415
4.78	0.0559	5.46	0.0365
4.83	0.0561	5.78	0.0226

Determination of K_3 , K_4 , K_6 , k_3 , k_4 , and k_6 . Decolourized acid solutions were mixed with acetate buffers and the rate of the restoring of the colour was determined. No reliable measurements could be performed at $\text{pH} > 6$, e.g. in phosphate buffers, since the carbinol precipitates owing to the reactions $S'' \rightarrow S' + H^+ \rightarrow C + 2 H^+$, and the equilibrium absorbancies are not known. Only a rough determination of k_3 was possible from kinetic measurements in borate buffers, $\text{pH} \approx 9$, where the reactions $B + H_2O \rightarrow S'$ and $B + OH^- \rightarrow C$ dominate, if a neutral dye solution is mixed with a borate buffer.

It proved possible to calculate the remaining constants from the results of the kinetic measurements in acetate buffers. Eqn. (3) was used and since K_1 , K_2 , k_5 and approximate values of k_1 and k_2 were known, it was possible to calculate approximate values of the remaining constants. By repeating the calculations refined values were obtained. The method of calculation was successfully tested on a dyestuff that permits reliable measurements, kinetic as well as equilibrium ones over large pH-ranges, and therefore could be treated with the methods of calculations used in previous investigations.

Table 4. *o*-IMG. Kinetic measurements in acetate buffers. $\lambda = 629 \text{ m}\mu$; $T = 20.0^\circ\text{C}$; $C_M = 5 \times 10^{-6} \text{ M}$.

pH	$k \text{ min}^{-1}$	pH	$k \text{ min}^{-1}$
3.44	0.0150	4.60	0.0792
3.57	0.0188	4.68	0.0823
3.67	0.0230	4.79	0.0828
3.76	0.0273	4.88	0.0826
3.92	0.0347	4.99	0.0798
4.03	0.0415	5.13	0.0748
4.14	0.0489	5.19	0.0706
4.24	0.0560	5.28	0.0617
4.33	0.0630	5.36	0.0549
4.42	0.0698	5.47	0.0402
4.52	0.0741		

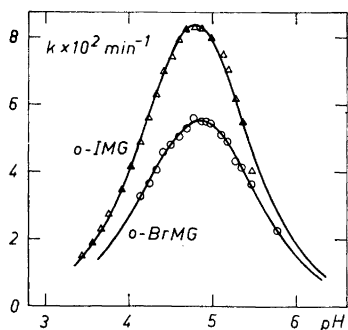


Fig. 4. *o*-BrMG and *o*-IMG. The rate constant k as a function of pH in the range pH 3.4–5.8. The points represented by the symbols Δ and \circ are obtained experimentally. The curves are calculated from the nonapproximated eqn. (3).

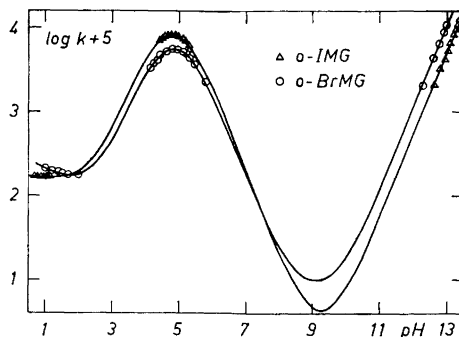


Fig. 5. *o*-BrMG and *o*-IMG. $\log k$ as a function of pH in the range pH 0.5–13.5. The curves are calculated from eqn. (3).

Fig. 4 shows the experimentally obtained k -values within the pH-range 3.4–5.8. The full drawn curves were calculated from the nonapproximated eqn. (3) and the following values were obtained:

o-Bromo MG: $K_3 = (3.5 \pm 0.1) \times 10^{-5}$ M; $K_4 = (5.6 \pm 0.2) \times 10^{-6}$ M;
 $K_6 = (1.55 \pm 0.10) \times 10^3$; $k_3 = (6.4 \pm 0.3) \times 10^{-5}$ min $^{-1}$;
 $k_4 = 0.099 \pm 0.002$ min $^{-1}$; $k_6 = (3.7 \pm 0.5) \times 10^{-6}$ min $^{-1}$.

o-Iodo MG: $K_3 = (3.4 \pm 0.1) \times 10^{-5}$ M; $K_4 = (7.3 \pm 0.4) \times 10^{-6}$ M;
 $K_6 = (8.5 \pm 1.1) \times 10^3$; $k_3 = (1.9 \pm 0.2) \times 10^{-5}$ min $^{-1}$;
 $k_4 = 0.159 \pm 0.004$ min $^{-1}$; $k_6 = (7.8 \pm 1.6) \times 10^{-6}$ min $^{-1}$.

In Fig. 5 $\log k$ is shown as a function of pH in the pH-range 0.5–13.5. The full drawn curves were calculated from eqn. (3).

Figs. 6 and 7 show the distribution at equilibrium of the five species of the dyes as a function of pH.

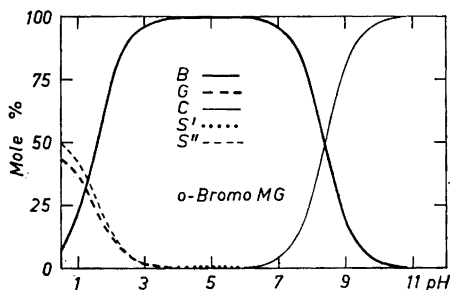


Fig. 6. *o*-BrMG. The distribution of the different species, at equilibrium, as a function of pH.

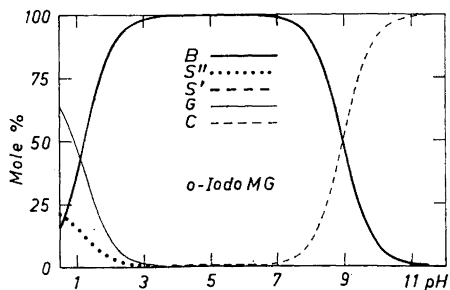


Fig. 7. *o*-IMG. The distribution of the different species, at equilibrium, as a function of pH.

Table 5. Corresponding values of the constants for a comparison between Malachite Green and its *ortho*-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	0.036	2.7	5.8	22	0.0147	
<i>o</i> -Fluoro MG	0.048	3.3	5.4	21.3	0.0149	
<i>o</i> -Chloro MG	0.045	4.3	3.2	1.76	0.00167	
<i>o</i> -Bromo MG	0.057	3.5	5.6	1.05	0.00064	
<i>o</i> -Iodo MG	0.078	3.4	7.3	0.27	0.00012	
Dyestuff	$k_1 \times 10^3$ (min ⁻¹)	$k_2 \times 10^3$ (min ⁻¹)	$k_3 \times 10^3$ (min ⁻¹)	k_4 (min ⁻¹)	k_5 (min ⁻¹)	$k_6 \times 10^6$ (M ⁻¹ min ⁻¹)
Malachite Green	168	7.8	6.5	0.44	31.7	4.6
<i>o</i> -Fluoro MG	54	2.53	2.35	0.157	10.7	1.7
<i>o</i> -Chloro MG	2.1	1.20	0.127	0.076	1.34	3.1
<i>o</i> -Bromo MG	1.29	1.23	0.064	0.099	1.08	3.7
<i>o</i> -Iodo MG	0.36	1.32	0.019	0.159	0.535	7.8

DISCUSSION

If the corresponding figures in Table 5 are compared, it can be found that there are great differences between Malachite Green and *o*-Fluoro MG on the one hand and *o*-Chloro MG, *o*-Bromo MG, and *o*-Iodo MG on the other as regards the hydration reactions $B + H_2O \xrightarrow{k_3} S'$ and $G + H_2O \xrightarrow{k_1} S''$.

The small *o*-fluoro substituent has only a minor influence on the rate of the hydration reactions, whereas the *o*-chloro, *o*-bromo and *o*-iodo substituents have a strong and increasing effect on both the hydration equilibria and the rate of the hydration reactions. This strong effect increases with the size of the substituent and is obviously mainly due to "steric hindrance" of the hydration reactions at the central methane carbon atom.

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REFERENCES

1. Cigén, R. *Protolysengleichgewichte und Reaktionsgeschwindigkeiten einiger basischer Triphenylmethanfarbstoffe* (Diss.), University, Lund 1956.
2. Cigén, R. *Acta Chem. Scand.* **15** (1961) 1892.
3. Cigén, R. *Acta Chem. Scand.* **15** (1961) 1905.
4. Cigén, R. and Bengtsson, G. *Acta Chem. Scand.* **16** (1962) 1837.
5. Cigén, R. and Ekström, C.-G. *Acta Chem. Scand.* **17** (1963) 1189.

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