Equilibrium and Kinetic Studies on Halide Derivatives of Malachite Green. I. *ortho*-Fluoro 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 *o*-Fluoro Malachite Green.

Three protolytic, two hydration, and six rate constants have been determined by spectrophotometric measurements in aqueous solutions with ionic strength 0.5 M at 20.0°C. A comparison with the values of the corresponding constants of Malachite Green shows that there is a marked difference between the rate constants, which are 3—4 times larger in Malachite Green than in the *o*-fluoro derivative, whereas the differences between the values of the remaining constants amount to 2—33 %.

It has been shown in earlier investigations of derivatives of Malachite Green (MG) that a substituent in the *ortho*-position to the central carbon atom in some cases has a very strong "*ortho*-effect" [1-2] on the hydration reactions indicated below (in Malachite Green is X = H). Whereas the effects, caused by a

coloured (blue-green)   colourless

coloured (yellow)   colourless
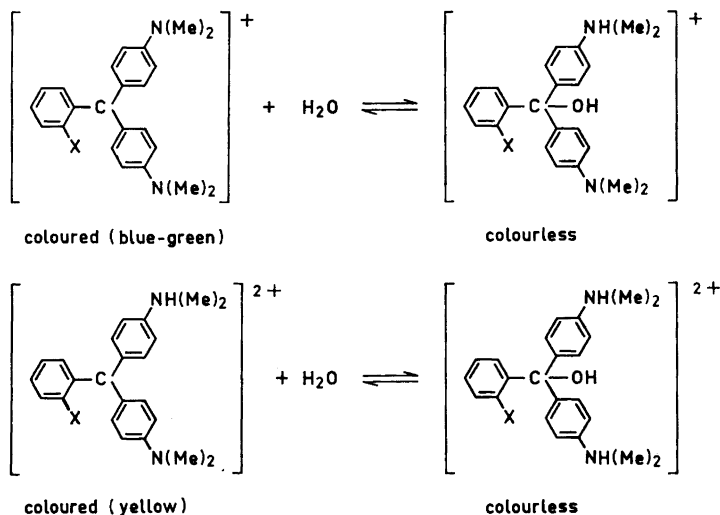
substituent on the reactions of the amino-groups, do not differ markedly, if the substituent is in the *para*-position or the *ortho*-position, the effects on the hydration reactions may be highly dependent on the position of the substituent. If the substituent X is $-Cl$ or $-NO_2$, the rate constants of the above mentioned hydration reactions from left to right, are 30—300 times larger for the *para*-derivatives than for the *ortho*-derivatives. Furthermore, the equilibria are strongly displaced towards the coloured species when the substituent is shifted from *para*- to *ortho*-position.

This "*ortho*-effect" is more pronounced for the bulky group $--NO_2$ than for $-Cl$. Preliminary investigations of *o*-bromo and *o*-iodo Malachite Green indicate that in these dyes the "*ortho*-effect" is of the same magnitude as in *o*-nitro Malachite Green. It is therefore interesting to investigate, if the small fluorine substituent in *o*-fluoro Malachite Green has any noticeable effect on the hydration reactions.

The protolytic and hydration equilibria and the rate constants of *o*-fluoro Malachite Green have been determined with the same methods as those used by one of the authors in previous investigations of similar dyes. The measurements were carried out spectrophotometrically in aqueous solutions, containing 2 % of acetone, with the constant ionic strength 0.5 M at 20.0°C.

A neutral or weakly acid aqueous solution of *o*-fluoro Malachite Green is blue. If it is made strongly acid, it instantaneously turns yellow and is then strongly decolourized owing to a slow hydration of the yellow species. If the neutral solution is made alkaline, pH > 9, it is completely decolourized owing to a slow reaction between the blue species and OH^--ions. The reactions may be written schematically in the following way, where
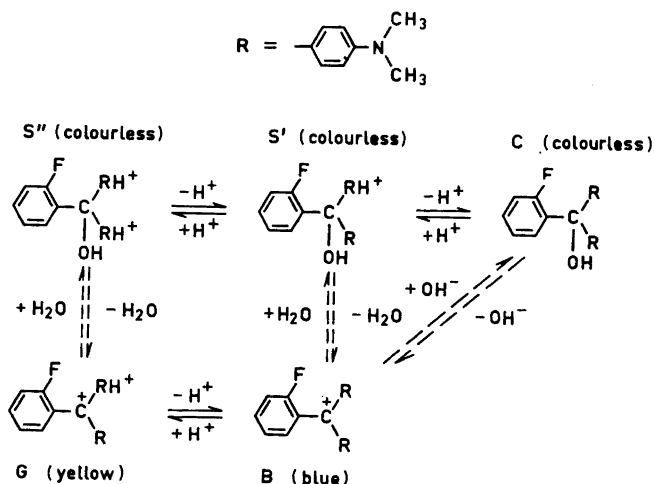
As to definitions of constants and symbols, *cf.* a previous article by one of the authors (*Acta Chem. Scand.* **15** (1961) 1894) [3].

＊ The equations used in this article are the same as in Ref.[3] and the numeration of the equations is also that of Ref.[3]

EXPERIMENTAL

Chemicals and solutions. o-*Fluoro Malachite Green.* The leuco compund was prepared in a nitrogen atmosphere by refluxing for 18 h o-fluorobenzaldehyde (from L. Light, Colnbrock, England) (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 bensene-ethanol. White needles, m.p. 131°C, were obtained. (Found: F 5.5. Calc. for $C_{23}H_{25}N_2F$: F 5.45). 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 61.7; H 5.7; N 6.5; Cl 7.8; F 4.1. Calc. for $C_{23}H_{24}O_4N_2ClF$: C 61.8; H 5.4; N 6.3; Cl 7.9; F 4.25).

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 there can be seen the absorption curves for the blue ion B in acetate buffer and for the yellow ion G in dilute hydrochloric acid. The molecular extinction cofficients were calculated from the experimentally obtained absorption curves and eqn. (3) ($e_B = C_M \cdot \varepsilon_B$ and $e_G = C_M \cdot \varepsilon_G$). The following values were obtained: $\lambda_{B\ max} = 633$ mμ and 422 mμ; $\varepsilon_{B\ max} = 9.6 \times 10^4$ and 1.50×10^4, respectively. $\lambda_{G\ max} = 435$ mμ; $\varepsilon_G = 2.3 \times 10^4$.

Determination of K_1. Equivalent volumes of the dye stock solution and of suitable HCl + KCl-buffers were mixed and the initial absorbancies, e_o, were determined by extrapolation of the absorbancies to $t = 0$. The measure-
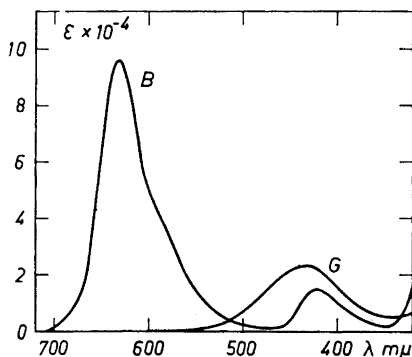

Fig. 1. o-Fluoro Malachite Green. Absorption curves. B is the curve of the blue-green ion $[(Me_2NC_6H_4)_2CC_6H_4F]^+$ in acetat buffer, G is the curve of the yellow ion
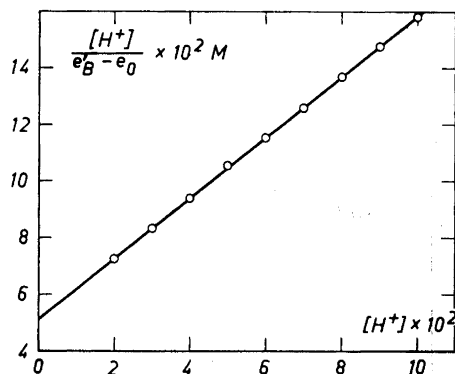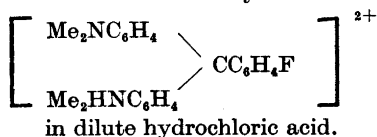
$$\begin{bmatrix} Me_2NC_6H_4 \\ \diagdown \\ \diagup \quad CC_6H_4F \\ Me_2HNC_6H_4 \end{bmatrix}^{2+}$$

in dilute hydrochloric acid.

Fig. 2. $[H^+]/(e'_B - e_o)$ plotted against $[H^+]$ for the determination of K_1.

Table 1. o-Fluoro Malachite Green. $e_O.$, $e_\infty.$, and k-values for the determination of K_1, K_2, and k_1. $C_M = 1 \times 10^{-5}$ M, $e_B = 0.960$, $e_B' = 0.940$, $e_G = 0.006$, $d = 1$ and 5 cm, $\lambda = 633$ mμ, $T = 20.0°C$.

[H$^+$] M	e_O	e_∞	K_2	k min^{-1}	k_1 min^{-1}
0.020	0.664	0.0880	22.7	0.0205	0.0539
0.030	0.580	0.0634	21.6	0.0253	0.0543
0.040	0.514	0.0486	21.4	0.0289	0.0543
0.050	0.466	0.0398	21.2	0.0317	0.0541
0.060	0.420	0.0334	21.2	0.0338	0.0538
0.070	0.385	0.0290	21.2	0.0356	0.0536
0.080	0.356	0.0256	21.0	0.0372	0.0537
0.090	0.330	0.0228	21.0	0.0389	0.0540
0.100	0.308	0.0208	20.8	0.0398	0.0536
Mean values			21.3		0.0539

$$k_2 = 0.00253 \text{ min}^{-1}$$

ments were carried out at the wavelength $\lambda = 633$ mμ. In Fig. 2 $[H^+]/(e_B'-e_o)$ is plotted against $[H^+]$. The slope l and the intercept y of the obtained straight line and eqn. (2) give $(e_B' = 0.940)$; $y = 0.0510$; $l = 1.071$; $K_1 = 21.0 \pm 0.3 \text{ M}^{-1}$.

Determination of K_2. The dye stock solution was mixed with HCl + KCl-buffers and the equilibrium absorbancies, e_∞, were determined. K_2 was calculated from eqn. (4) and the results are recorded in Table 1. From this table the mean value $K_2 = 21.3 \pm 0.6$ is obtained.

Kinetic measurements. If the dye stock solution is mixed with NaOH + KCl-buffers, the solutions are decolourized at a rate that is directly proportional to $[OH^-]$. In Fig. 3 the rate constants of the decolourization are plotted as a function of $[OH^-]$. A straight line is obtained which passes almost through the origin. This means that in the used pH-range $k_3 + k_6 \ll k_5$.oh. Therefore, only k_5 can be determined from Fig. 3; $k_5 = 10.7 \pm 0.2 \text{ min}^{-1} \text{ M}^{-1}$.
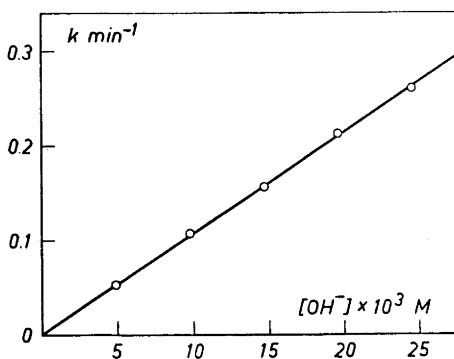

Fig. 3. The rate constant k as a function of $[OH^-]$ for the determination of k_5.
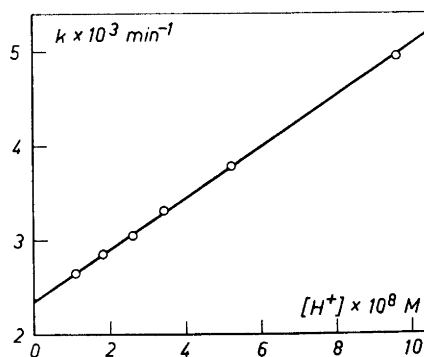
Fig. 4. The rate constant k as a function of $[H^+]$ in the pH-range 7 — 8 for the determination of k_3.

The rate constant k_3 was determined from kinetic measurements in phosphate buffers, pH 7.0—8.0. The approximate eqn. (10) can be used in this pH-range. In Fig. 4, k is plotted as a function of $[H^+]$. From the straight line $k_3 = 0.00235 \pm 0.00002$ min^{-1} is obtained.

Determination of k_1 *and* k_2. These rate constants were determined by kinetic measurements in HCl + KCl-buffers. The fading rate was determined, and to begin with, approximate values of k_1 and k_2 were calculated from eqn. (7). Table 1 contains the k-values and the more refined values of k_1 and k_2, which were calculated later from eqn. (6); $k_1 = 0.0539 \pm 0.0006$ min^{-1}; $k_2 = 0.00253 \pm 0.00007$ min^{-1}.

Determination of k_4, 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. The dye stock solution was partially decolourized by making it 0.02 M with respect to hydrochloric acid. Then the following reactions occur in the forward direction ($\rightarrow$): B + H$^+$ + H$_2$O $\rightleftharpoons$ G + H$_2$O $\rightleftharpoons$ S$''$ and B + H$^+$ + H$_2$O $\rightleftharpoons$ S$'$ + H$^+$ $\rightleftharpoons$ S$''$ This partially decolourized dye solution was then mixed with acetate buffers and the colour was more or less restored owing to the abovementioned reactions in the reverse direction. The rate constants, k, for the restoring of the colour were determined.

In Fig. 5, k is plotted as a function of pH. The curve has a maximum, $k_{max} = 0.090$ min^{-1}, when pH = 4.875. It has been shown before (*cf.* Ref.[3]) that $[H^+]_{k\ max} = \sqrt{K_3K_4}$ can be used as a good approximation. The constant K_3 can be calculated from the following equation (*cf.* Ref.[4] p. 1908)

$$k_{max} = \left(\frac{K_6}{K_4} \cdot \frac{K_3K_4}{K_3 + 2\sqrt{K_3K_4}} + 1\right)k_3$$

since k_{max}, k_3, and K_3K_4 are known. Furthermore, $K_6/K_4 = 1/K_1K_2K_3K_4$, by definition, and K_1K_2 is known. K_6K_4 can also be obtained from Fig. 4
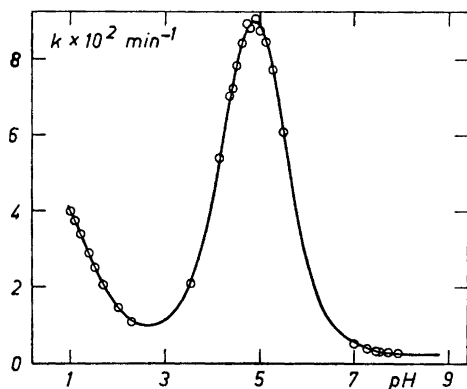

Fig. 5. The total rate constant k as a function of pH. The points represented by the symbols are obtained experimentally. The curve is calculated from the non-approximated eqn. (6).
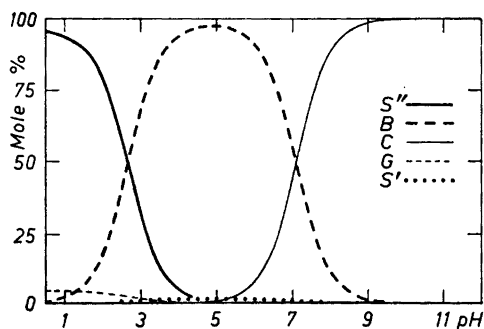

Fig. 6. The distribution of *o*-Fluoro Malachite Green between the different species as a function of pH.

Table 2. A comparison between the values of the corresponding constants of Malachite Green and its o-Fluoro and o-Chloro derivatives.

	K_1	K_2	$K_3 \times 10^5$	$K_4 \times 10^6$	K_6	$k_1 \times 10^3$	$k_2 \times 10^4$	$k_3 \times 10^4$	$k_4 \times 10^2$
Malachite Green	28	22	2.7	5.8	68	168	78	65	44
o-Fluoro MG	21.0	21.3	3.3	5.4	67	54	25	23.5	15.7
o-Chloro MG	22.1	1.76	4.3	3.2	600	2.10	12.0	1.27	7.6

$(K_6/K_4 = (1.16 \pm 0.15) \times 10^7)$ but this figure does not give a reliable value of K_6/K_4.

From $pH_{k \; max} = 4.875$ we obtain $K_3K_4 = 1.78 \times 10^{-10} \; M^2$ which value, combined with $K_1 = 21.0$ and $K_2 = 21.3$, gives $K_6/K_4 = 1.26 \times 10^7 \; M^{-1}$. Then K_3 is calculated from the equation above. $\mathbf{K_3 = (3.3 \pm 0.2) \times 10^{-5} \; M}$. $\mathbf{K_4 = (5.4 \pm 0.6) \times 10^{-6} \; M}$ is calculated from the value of $K_3K_4 = 1.78 \times 10^{-10}$ and $\mathbf{K_6 = 67 \pm 5}$ from $K_6/K_4 = 1.26 \times 10^7$.

The remaining rate constants, k_4 and k_6, are calculated from $k_4 = k_3K_6$, which gives $\mathbf{k_4 = 0.157 \pm 0.006 \; min^{-1}}$ and from $k_6 = k_5K_wK_6/K_4$, which gives $\mathbf{k_6 = (1.7 \pm 0.2) \times 10^{-6} \; min^{-1}}$

The distribution at equilibrium between the five species B, G, C, S', and S" as a function of pH is shown in Fig. 6. The curves of the figure are calculated from the values of the constants reported above.

DISCUSSION

If the values of the constants of Malachite Green and o-Fluoro Malachite Green are compared, it can be seen in Table 2 that the o-fluoro substituent of the amino free phenyl ring does not influence the hydration equilibria — K_2 and K_6 are not changed — but the rates of the hydration reactions. The values of the rate constants of Malachite Green are constantly three times larger than the corresponding values of o-fluoro Malachite Green. Since the fluoro-substituent is small, no strong "steric hindrance" of the hydration reaction was expected. A comparison between the rate constants of the reactions

$G + H_2O \xrightarrow{k_1} S''$ and $B + H_2O \xrightarrow{k_3} S'$ of o-Fluoro MG, o-Chloro MG and Malachite Green (see Table 2) shows that the hydration reactions are markedly more hindered by the larger o-chloro substituent than by the smaller o-fluoro one, owing to the stronger "steric hindrance"-effect of the o-chloro substituent. It can be expected that o-Bromo MG and o-Iodo MG have still stronger "ortho-effects" than o-Chloro MG and a thorough investigation of the o-bromo and o-iodo derivatives of Malachite Green is planned.

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