

# The Application of Linear Free Energy Relationships on Derivatives of Malachite Green. Equilibrium and Kinetic Studies on *m*-Fluoro and *m*-Nitro Malachite Green

CARL-GUSTAV EKSTRÖM

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

The series of investigations of protolytic and hydration equilibria and reaction rates of basic triphenylmethane dyes is continued with the investigations of *m*-Fluoro and *m*-Nitro Malachite Green. Three protolytic, two hydration, and six rate constants have been determined at 20°C by spectrophotometric measurements for each dye in aqueous solutions of ionic strength 0.5 M.

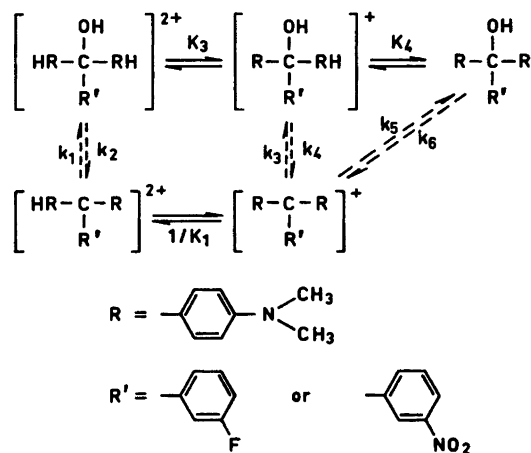
The result of these investigations, and also of those previously reported as parts of this series, have been analyzed with the aid of linear free energy relationships. This method of analysis has provided strong support for the assumed reaction mechanisms.

## EQUILIBRIUM AND KINETIC STUDIES ON *m*-FLUORO AND *m*-NITRO MALACHITE GREEN

*m*-Fluoro and *m*-Nitro Malachite Green (*m*-F-MG and *m*-NO<sub>2</sub>-MG, resp.) react in a manner similar to that of Malachite Green<sup>1,2</sup> and most of the other *meta* and *para* derivatives of Malachite Green previously investigated.<sup>2,12,13,15</sup> The solubility of the carbinols are such that reliable measurements in the pH range 6-8 can be performed only when the total concentrations of the dyestuffs are so low as  $2 \times 10^{-6}$  M. Neutral aqueous solutions of the dyestuffs are blue-green, but if these are made strongly acid, the colour momentarily changes to yellow and then slowly fades. In alkaline solutions the dyestuffs are totally decolourized.

## EXPERIMENTAL

*m*-Fluoro Malachite Green. The leuco compound was prepared by refluxing for 20 h in a nitrogen atmosphere a solution of *m*-fluorobenzaldehyde, dimethylaniline, urea, and conc. hydrochloric acid in ethanol. After purifying and recrystallization from ethanol the leuco compound was obtained as white needles, m.p. 99.5-100.5°C (*cf.* Ref. 9, in which m.p. 99-100°C is reported). The dyestuff was prepared by oxidizing the leuco compound,



Scheme 1

dissolved in a calculated amount of 5 M HCl and diluted with 10 % acetic acid. Lead dioxide was used as the oxidizing agent. From the oxidized product the perchlorate was prepared and was obtained as small green crystals after repeated recrystallizations from water. (Found: C 62.6; H 5.66; N 6.01; F 3.99; Cl 7.79. Calc. C 61.80; H 5.42; N 6.27; F 4.25; Cl 7.94).

*m*-Nitro Malachite Green was prepared in the same manner as the *m*-fluoro derivative. The leuco compound was obtained as white needles, m.p. 153°C, and the perchlorate of the dyestuff as a reddish brown powder. (Analysis of the perchlorate. Found: C 58.3; H 5.02; N 8.16; O 21.4; Cl 7.13. Calc. C 58.29; H 5.10; N 8.87; O 20.26; Cl 7.48).

### Measurements, calculations, and results

The absorption curves of the two dyestuffs have been drawn in Figs. 1 and 2. The wavelengths at the absorption maxima and the molar extinction coefficients at these wavelengths have been determined and the results are tabulated in Table 1.

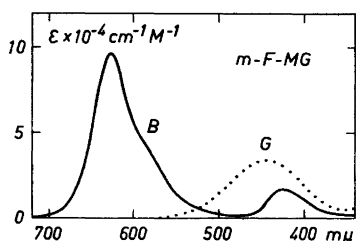


Fig. 1. *m*-F-MG. Absorption curves. *B* is the curve of the bluegreen ion  $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{F}]^+$  in acetate buffer. *G* is the curve of the yellow ion  $[(\text{Me}_2\text{NC}_6\text{H}_4)(\text{Me}_2\text{HNC}_6\text{H}_4)\text{CC}_6\text{H}_4\text{F}]^{2+}$  in dilute hydrochloric acid.

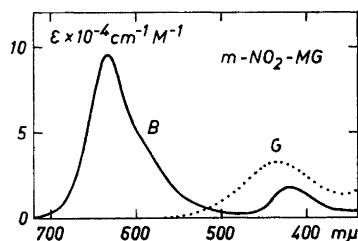


Fig. 2. *m*-NO<sub>2</sub>-MG. Absorption curves. *B* is the curve of the bluegreen ion  $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{NO}_2]^+$  in acetate buffer. *G* is the curve of the yellow ion  $[(\text{Me}_2\text{NC}_6\text{H}_4)(\text{Me}_2\text{HNC}_6\text{H}_4)\text{CC}_6\text{H}_4\text{NO}_2]^{2+}$  in dilute hydrochloric acid.

Table 1. The wavelengths and the molar extinction coefficients at the absorption maxima of the absorption curves of *m*-F- and *m*-NO<sub>2</sub>-MG.

Dyestuff	Species B		Species G	
	$\lambda$ m $\mu$	$\epsilon \times 10^{-4}$ cm <sup>-1</sup> M <sup>-1</sup>	$\lambda$ m $\mu$	$\epsilon \times 10^{-4}$ cm <sup>-1</sup> M <sup>-1</sup>
<i>m</i> -F-MG	424	1.7	444	3.4
	626	9.7		
<i>m</i> -NO <sub>2</sub> -MG	422	1.8	432	3.3
	633	9.5		

Table 2. Obtained values of the initial absorbancy,  $e_0$ , in HCl-KCl buffers.  
 $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$  m $\mu$  (*m*-F) and 633 m $\mu$  (*m*-NO<sub>2</sub>).

[H <sup>+</sup> ] M	$e_0$	
	<i>m</i> -F-MG	<i>m</i> -NO <sub>2</sub> -MG
0.01	0.727	0.682
2	621	618
3	552	565
4	491	513
5	442	477
6	408	444
7	374	412
8	343	379
0.09	0.324	0.365

Table 3. Obtained values of the equilibrium absorbancy,  $e_\infty$ , in HCl-KCl buffers.  
 $C_M = 1.0 \times 10^{-5}$  M;  $d = 5$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$  m $\mu$  (*m*-F) and 633 m $\mu$  (*m*-NO<sub>2</sub>).

[H <sup>+</sup> ] M	$e_\infty$	
	<i>m</i> -F-MG	<i>m</i> -NO <sub>2</sub> -MG
$2 \times 10^{-5}$	0.862	0.774
0.01	0.0656	0.0425
2	344	219
3	230	146
4	174	110
5	142	89
6	120	75
7	102	64
8	88	—
9	0.0080	50
0.10	—	0.0045

Table 4. Obtained values of the equilibrium absorbancy,  $e_{\infty}$ , in acetate and phosphate buffers.  $C_M = 0.2 \times 10^{-5}$  M;  $d = 5$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$  m $\mu$  (*m*-F) and 633 m $\mu$  (*m*-NO<sub>2</sub>).

pH	$e_{\infty}$	
	<i>m</i> -F-MG	<i>m</i> -NO <sub>2</sub> -MG
3.42	0.623	0.495
3.65	705	587
3.89	768	662
4.13	805	705
4.50	838	740
4.78	843	742
4.98	835	732
5.26	826	695
5.46	798	667
5.81	737	543
6.04	663	444
6.43	495	269
6.79	317	1445
7.00	224	965
7.26	1400	555
7.44	970	375
7.55	780	295
7.69	560	205
7.81	0.0430	0.0150

Table 5. Obtained values of the rate constant of the over-all reaction,  $k$ , in HCl-KCl buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$  m $\mu$  (*m*-F) and 633 m $\mu$  (*m*-NO<sub>2</sub>).

[H <sup>+</sup> ] mM	$k \times 10^3 \text{ min}^{-1}$	
	<i>m</i> -F-MG	<i>m</i> -NO <sub>2</sub> -MG
10	3.26	1.93
20	4.90	2.95
30	6.14	3.80
40	7.15	4.52
50	7.94	5.13
60	8.62	5.57
70	9.13	6.05
80	9.74	6.42
90	10.05	6.68

Table 6. Obtained values of the rate constant of the over-all reaction,  $k$ , in acetate and phosphate buffers.  $C_M = 1.0 \times 10^{-5}$  M (acetate) and  $0.29 \times 10^{-5}$  M (phosphate);  $d = 1$  cm (acetate) and 3 cm (phosphate);  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$   $\mu\text{m}$  ( $m\text{-F}$ ) and 633  $\mu\text{m}$  ( $m\text{-NO}_2$ ).

pH	$k \times 10^2 \text{ min}^{-1}$	
	$m\text{-F-MG}$	$m\text{-NO}_2\text{-MG}$
3.25	1.80	1.10
3.55	2.47	1.41
3.75	3.21	1.78
4.03	4.69	2.47
4.23	6.02	2.99
4.42	7.28	3.40
4.50	7.82	—
4.60	8.11	3.61
4.69	8.35	3.65
4.78	8.36	3.67
4.88	8.24	3.59
4.99	8.14	3.43
5.06	7.68	3.31
5.12	7.82	3.14
5.21	6.94	2.91
5.30	6.80	2.70
5.41	5.96	—
5.53	5.43	—
5.60	4.91	—
5.70	4.26	—
5.80	3.79	—
7.01	0.873	0.624
7.12	0.843	0.605
7.27	0.790	0.592
7.45	0.745	0.590
7.56	0.733	0.568
7.76	—	0.562
7.83	0.692	—

Table 7. Obtained values of the rate constant of the over-all reaction,  $k$ , in NaOH—KCl buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 626$   $\mu\text{m}$  ( $m\text{-F}$ ) and 633  $\mu\text{m}$  ( $m\text{-NO}_2$ ).

[OH <sup>-</sup> ] mM	$k \times 10^2 \text{ min}^{-1}$	
	$m\text{-F-MG}$	$m\text{-NO}_2\text{-MG}$
1.16	—	7.42
2.31	8.80	16.83
3.47	—	27.6
4.63	18.43	32.7
5.79	25.2	44.5
6.94	29.6	53.8
9.26	39.7	—
11.57	49.5	—

Table 8. Obtained values of the constants and their error limits of *m*-F- and *m*-NO<sub>2</sub>-MG together with the values of the constants of MG.

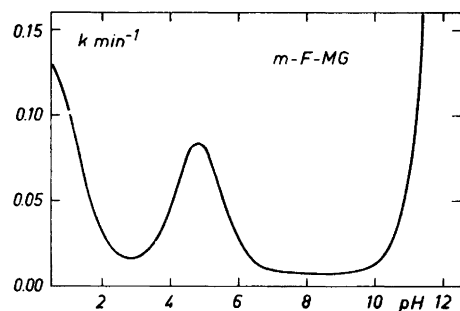
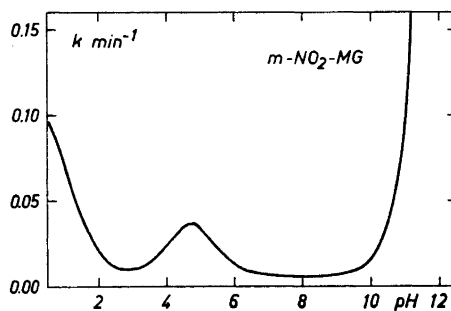
## Equilibrium constants

	protolytic			hydration	
	$10^2 \times 1/K_1$ M	$10^5 \times K_3$ M	$10^6 \times K_4$ M	$K_2$	$10^3 \times 1/K_6$
MG	3.6	2.7	5.8	22	14.7
<i>m</i> -F-MG	$5.4 \pm 0.1$	$3.5 \pm 0.2$	$5.7 \pm 0.3$	$70 \pm 1$	$47 \pm 2$
<i>m</i> -NO <sub>2</sub> -MG	$8.0 \pm 0.2$	$4.1 \pm 0.2$	$8.6 \pm 0.5$	$159 \pm 4$	$91 \pm 4$

## Rate constants

	coloured → colourless			colourless → coloured		
	$10^3 \times k_1$ min <sup>-1</sup>	$10^3 \times k_3$ min <sup>-1</sup>	$k_5$ M <sup>-1</sup> min <sup>-1</sup>	$10^3 \times k_2$ min <sup>-1</sup>	$10 \times k_4$ min <sup>-1</sup>	$10^6 \times k_6$ min <sup>-1</sup>
MG	16.8	6.5	31.7	7.8	4.4	4.6
<i>m</i> -F-MG	$15.3 \pm 0.3$	$6.63 \pm 0.07$	$44.5 \pm 0.9$	$2.20 \pm 0.08$	$1.40 \pm 0.05$	$2.1 \pm 0.3$
<i>m</i> -NO <sub>2</sub> -MG	$12.1 \pm 0.3$	$5.47 \pm 0.06$	$79 \pm 3$	$0.76 \pm 0.04$	$0.60 \pm 0.02$	$1.3 \pm 0.2$

Measurements of  $e_0$ ,  $e_\infty$ , and  $k$  HCl—KCl buffers (Tables 2, 3, and 5),  $e_\infty$ , and  $k$  in acetate and phosphate buffers (Tables 4 and 6), and  $k$  in NaOH—KCl buffers (Table 7) have been performed as previously reported.<sup>5,12</sup> The calculations of the sought constants and their error limits were carried out with the aid of a least square method as in Refs. 12 and 13. The obtained values of these constants together with the corresponding values of the constants for MG are listed in Table 8. The rate constant of the over-all reaction and the distri-

Fig. 3. *m*-F-MGFig. 4. *m*-NO<sub>2</sub>-MG

The rate constant of the over-all reaction,  $k$ , as functions of pH.

bution of the different species at equilibrium as functions of pH have been drawn in Figs. 3, 4, 5, and 6.

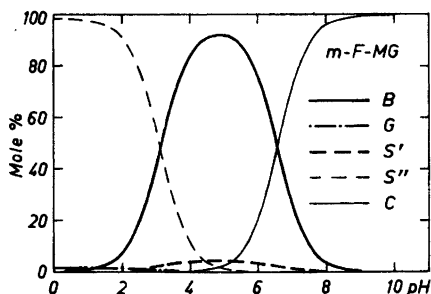


Fig. 5. *m*-F-MG

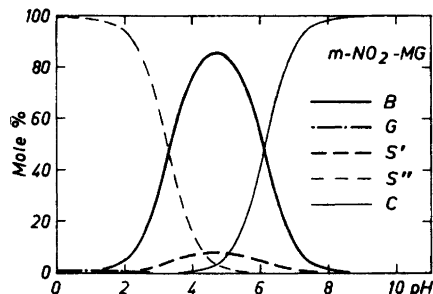


Fig. 6. *m*-NO<sub>2</sub>-MG

The distribution of the dye between the different species as functions of pH at equilibrium.

#### THE APPLICATION OF LINEAR FREE ENERGY RELATIONSHIPS

So far 27 different dyestuffs belonging to the class of mono substituted derivatives of Malachite Green have been investigated. One of these, Crystal Violet,<sup>10</sup> has a basic group,  $-\text{N}(\text{CH}_3)_2$ , while three others, the hydroxy derivatives of Malachite Green,<sup>2,5,11</sup> have an acid group,  $-\text{OH}$ , as a substituent. The remaining 23 dyestuffs have substituents, which do not make any expansion of the simple reaction scheme necessary. These 23 dyestuffs are: *o*-,<sup>14</sup> *m*-, and *p*-F-MG,<sup>15</sup> *o*-,<sup>2</sup> *m*-,<sup>13</sup> and *p*-Cl-MG,<sup>2</sup> *o*-,<sup>7</sup> *m*-,<sup>13</sup> and *p*-Br-MG,<sup>15</sup> *o*-,<sup>7</sup> *m*-,<sup>13</sup> and *p*-I-MG,<sup>15</sup> *o*-,<sup>12</sup> *m*-,<sup>12</sup> and *p*-CH<sub>3</sub>-MG,<sup>12</sup> *o*-,<sup>2</sup> *m*-, and *p*-NO<sub>2</sub>-MG,<sup>2</sup> *o*-,<sup>16</sup> *m*-,<sup>5</sup> and *p*-OCH<sub>3</sub>-MG,<sup>2</sup> *p*-N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>-MG (Methyl Green),<sup>2</sup> and unsubstituted Malachite Green.<sup>1,2</sup>

Not all of the rate constants can be determined by direct measurements. By rewriting the expression for the observed over-all rate constant:

$$k_{\text{obs}} = \frac{k_1}{1 + \frac{1}{K_1 h}} + \frac{k_2}{1 + \frac{K_3}{h} + \frac{K_3 K_4}{h^2}} + \frac{k_3}{1 + K_1 h} + \frac{k_4}{1 + \frac{h}{K_3} + \frac{K_4}{h}} + \frac{k_5 \text{oh}}{1 + K_1 h} + \frac{k_6}{\frac{h}{K_4} + \frac{h^2}{K_3 K_4}} = \sum_{i=1}^6 f_i$$

and plotting  $f_i/k_i$  against pH for given values of the protolytic constants (these do not change very much from one dye to another), one can easily see in which pH range a certain term will predominate and hence where the corresponding rate constants might be determined with the greatest possible precision, provided that the magnitude of the rate constants of the dyestuff in question are known. It will be seen (Fig. 7) that  $k_1$  or  $k_2$  can be measured

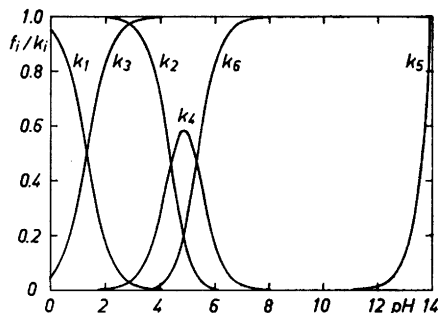


Fig. 7. The coefficients  $f_i/k_i$  of the terms in the rewritten expression for the over-all rate constant as functions of pH. The values  $K_1 = 20 \text{ M}^{-1}$ ;  $K_3 = 4 \times 10^{-5} \text{ M}$ ; and  $K_4 = 5 \times 10^{-6} \text{ M}$  were used in the calculations.

in acid solutions (pH 0–2),  $k_3$  in weakly alkaline (pH 7–9),  $k_4$  in weakly acid (pH 4–6), and  $k_5$  in alkaline solutions (pH 11–14).  $k_6$  cannot be measured in any range since its value is only about 0.1 % of the value of  $k_3$ .

The computation of the constants have in principle been performed in the following way: The term, which contains the rate constant in question is set equal to  $k_{\text{obs}}$  (if necessary corrected with the values of the other terms). This expression is rewritten to a polynomial in  $h$ , and the polynomial constants are computed with the aid of a least square method. From these it is easy derive the required constants.

Example. Computation of  $k_4$ .

$$\frac{k_4}{1 + \frac{h}{K_3} + \frac{K_4}{h}} = k' = k_{\text{obs}} - \sum_{i \neq 4} f_i$$

$$\frac{k'}{h} = \frac{K_4}{k_4} + \frac{1}{k_4} \cdot h + \frac{1}{K_3 k_4} \cdot h^2 = a_0 + a_1 \cdot h + a_2 h^2$$

$$k_4 = 1/a_1; K_3 = a_1/a_2; K_4 = a_0/a_1$$

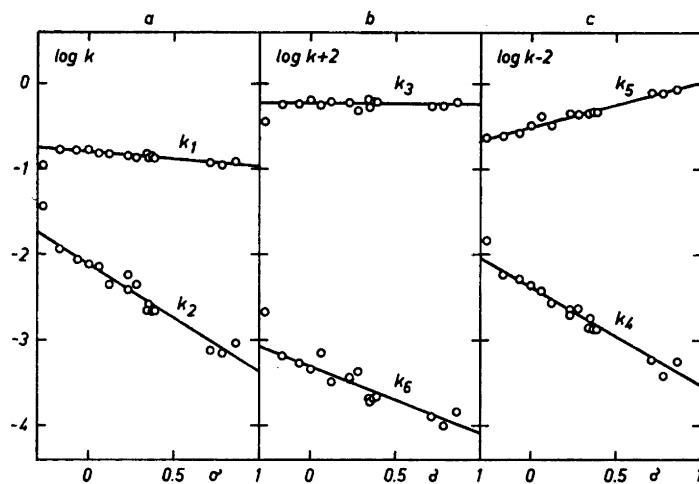
To verify the assumed reaction scheme, the obtained results have been analyzed with the aid of different forms of linear free energy relationships. Of the 23 dyestuffs mentioned earlier, those which have the substituent in the *meta* or *para* position have been selected for Hammett plots. For each of the eleven constants for any one dyestuff, the logarithm of the constant have been plotted against the Hammett substituent parameter  $\sigma$  (the values of  $\sigma$  according to Jaffé<sup>17</sup> can be found in Table 9). It will be seen that, apart from the points corresponding to *p*-OCH<sub>3</sub>-MG (only in certain of the diagrams, cf. Ref. 9), all points in each diagram are closely gathered together and form a straight line (Fig. 8). From these diagrams  $\log K_0$  and  $\rho$  have been computed with a least square method and the results are collected in Table 10.

Specific substituent effects have been examined according to a method due to van Bekkum, Verkade, and Webster.<sup>18</sup>  $\rho$  and  $K_0$  have been determined



Table 9. Values of the substituent parameter  $\sigma$ .

Substituent	According to Jaffé	According to van Bekkum <i>et al.</i>			
		primary	secondary ( $\sigma^n$ )	calculated from $\rho$ and $K_0$ for reactions with $ \rho  > 0.5$ ( $\sigma_c$ )	$\sigma_c - \sigma^n$
<i>p</i> -OH	—	—	-0.178	$-0.676 \pm 0.142$	0.498
<i>p</i> -CH <sub>3</sub>	-0.170	—	-0.129	$-0.137 \pm 0.041$	0.008
<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	—	—	-0.127	$-1.53 \pm 0.59$	1.40
<i>p</i> -OCH <sub>3</sub>	-0.268	—	-0.111	$-0.552 \pm 0.225$	0.441
<i>m</i> -CH <sub>3</sub>	-0.069	-0.069	—	—	—
H	0.000	0.000	—	—	—
<i>p</i> -F	0.062	—	0.056	$0.014 \pm 0.150$	0.042
<i>m</i> -OCH <sub>3</sub>	0.115	—	0.076	$0.144 \pm 0.034$	0.068
<i>m</i> -OH	—	—	0.095	$0.140 \pm 0.028$	0.045
<i>p</i> -Cl	0.227	—	0.238	$0.179 \pm 0.106$	0.059
<i>p</i> -Br	0.232	—	0.265	$0.201 \pm 0.064$	0.064
<i>p</i> -I	0.276	—	0.299	$0.152 \pm 0.093$	0.147
<i>m</i> -F	0.337	0.337	—	—	—
<i>m</i> -I	0.352	0.352	—	—	—
<i>m</i> -Cl	0.373	0.373	—	—	—
<i>m</i> -Br	0.391	0.391	—	—	—
<i>m</i> -NO <sub>2</sub>	0.710	0.710	—	—	—
<i>p</i> -NO <sub>2</sub>	0.778	0.778	—	—	—
<i>p</i> -N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	0.859	—	0.800	$0.687 \pm 0.079$	0.113

Fig. 8.  $\log k$  as functions of Jaffé's  $\sigma$  values, concerning the rate constants a)  $k_1$  and  $k_2$ , b)  $k_3$  and  $k_6$ , c)  $k_4$  and  $k_5$ .

from "primary"  $\sigma$  values for *m*-CH<sub>3</sub>, H, *m*-F, *m*-Cl, *m*-Br, *m*-I, *m*-NO<sub>2</sub>, and *p*-NO<sub>2</sub> (see Tables 9 and 10). With these values,  $\sigma$  values for the other substituents have been calculated (Table 9). Only such reactions, which have

Table 10. Values of  $\rho$  and  $K_0$  in the Hammett equation  $\log K = \log K_0 + \sigma\rho$ .

Reaction corresp. to the constant:	Experimental values of $K_0$ (MG)	Calculated values of $K_0$ and $\rho$ , from a plot of $\log K$ against $\sigma$ .			
		$\sigma$ according to Jaffé		$\sigma$ according to Bekkum	
		$K_0$	$\rho$	$K_0$	$\rho$
$K_1^{-1} \times 10^2$	3.58	4.6 $\pm$ 0.2	0.24 $\pm$ 0.04	4.1 $\pm$ 0.3	0.36 $\pm$ 0.04
$K_3 \times 10^5$	2.7	3.2 $\pm$ 0.2	0.28 $\pm$ 0.07	2.8 $\pm$ 0.2	0.37 $\pm$ 0.04
$K_4 \times 10^6$	5.8	5.4 $\pm$ 0.3	0.18 $\pm$ 0.06	5.8 $\pm$ 0.9	0.18 $\pm$ 0.10
$K_2 \times 10^{-1}$	2.2	2.1 $\pm$ 0.2	1.08 $\pm$ 0.09	2.3 $\pm$ 0.2	1.14 $\pm$ 0.06
$K_5^{-1} \times 10^2$	1.47	1.45 $\pm$ 0.11	1.14 $\pm$ 0.08	1.4 $\pm$ 0.2	1.23 $\pm$ 0.09
$k_1 \times 10$	1.68	1.60 $\pm$ 0.03	-0.17 $\pm$ 0.02	1.67 $\pm$ 0.05	-0.21 $\pm$ 0.02
$k_3 \times 10^3$	6.47	5.9 $\pm$ 0.2	-0.01 $\pm$ 0.03	6.2 $\pm$ 0.4	-0.06 $\pm$ 0.04
$k_5 \times 10^{-1}$	3.17	3.09 $\pm$ 0.10	0.53 $\pm$ 0.03	2.9 $\pm$ 0.1	0.57 $\pm$ 0.03
$k_2 \times 10^3$	7.83	7.6 $\pm$ 0.6	-1.25 $\pm$ 0.08	7.4 $\pm$ 0.4	-1.36 $\pm$ 0.04
$k_4 \times 10$	4.40	4.1 $\pm$ 0.2	-1.15 $\pm$ 0.06	4.4 $\pm$ 0.3	-1.29 $\pm$ 0.05
$k_6 \times 10^6$	4.6	4.9 $\pm$ 0.5	-0.78 $\pm$ 0.10	4.4 $\pm$ 0.4	-0.82 $\pm$ 0.05

$|\rho| > 0.5$ , e.g. those reactions corresponding to the constants  $K_2$ ,  $K_6$ ,  $k_2$ ,  $k_4$ ,  $k_5$ , and  $k_6$ , have been used. The  $\sigma$  values obtained in this way, have been compared with  $\sigma^a$  values according to van Bekkum *et al.* (Table 9). It can be seen that only in the cases of Crystal Violet, the *p*-OH, and *p*-OCH<sub>3</sub> derivatives of Malachite Green are there significant differences between  $\sigma$  and  $\sigma^a$ . For these derivatives the *para* resonance energy,  $\Delta\Delta F_p$ , have been calculated (see Table 11), and the values plotted against  $\rho$ .

The value of  $\Delta\Delta F_p$  is suggested as a measure of the differences in direct conjugation between initial and final (or transition) states.<sup>19</sup> For Crystal Violet the values of  $|\Delta\Delta F_p|$  range from 1 to 3 kcal per mole and have signs indicating that the coloured ions of the dye are the favoured states.

Table 11. The *para* resonance energy,  $\Delta\Delta F_p$ , calculated from the formula:  $\Delta\Delta F_p = -2.303 RT(\sigma - \sigma^a)\rho$ , where  $2.303 RT = 1.34$  kcal per mole at 20°C. The constants A and B refer to the expression:  $\Delta\Delta F_p = A + B\rho$ .

Reaction, corresponding to the constant	$\rho$	$\Delta\Delta F_p$ (kcal/mole)		
		<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> -MG	<i>p</i> -OH-MG	<i>p</i> -OCH <sub>3</sub> -MG
$k_2 \times 10^3$	-1.36	-1.70	-0.77	-0.73
$k_4 \times 10$	-1.29	-0.81	-0.53	-0.52
$k_5 \times 10^6$	-0.82	-1.89	—	-0.80
$k_6 \times 10^{-1}$	0.57	1.05	—	0.04
$K_2 \times 10^{-1}$	1.14	3.62	1.03	0.99
$K_6^{-1} \times 10^2$	1.23	2.49	0.96	0.85
A		0.7	0.2	0.1
B		1.8	0.7	0.6

Table 12. Values of the polar substituent parameter,  $\sigma^*$ , and the steric parameter,  $E_s$ , according to Taft.

Substituent	$\sigma^*$	$E_s$
F	0.24	0.49
Cl	0.20	0.18
Br	0.21	0.01
I	0.21	-0.20
CH <sub>3</sub>	-0.17	0.00
NO <sub>2</sub>	0.80	-0.71
OCH <sub>3</sub>	-0.39	0.97

Table 13. Calculated values of the reaction parameter  $\delta$  in the formula:  
 $\log k/k_0 = \sigma^* \cdot \rho + E_s \delta$ .

Reaction corresponding to the constant:	$\rho$	$\delta$
$1/K_1$	0.36	0.0
$K_3$	0.37	-0.0
$K_4$	0.18	-0.1
$K_5$	1.14	1.6
$1/K_6$	1.23	1.7
$k_1$	-0.21	1.6
$k_3$	-0.06	1.5
$k_5$	0.57	0.8
$k_2$	-1.36	0.1
$k_4$	-1.29	-0.2
$k_6$	-0.82	-0.7

#### Correlation of *ortho* derivatives according to Taft.<sup>19,20</sup>

$$\log k/k_0 = \sigma^* \cdot \rho + E_s \cdot \delta$$

$k$  = the constant of the *ortho* derivative

$k_0$  and  $\rho$  have been obtained from a Hammett plot against primary  $\sigma$  values

$\sigma^*$  = the polar contribution to the substituent effect (Table 12)

$E_s$  = steric parameter, achieved by Taft for *ortho* substituted benzoates (see Table 12)

$\delta$  = reaction parameter showing the sensitivity of the reaction for steric effect.

For the *ortho* halids, *o*-methyl, and *o*-methoxy derivatives ( $\log k/k_0 - \sigma^* \cdot \rho$ ) are computed and plotted against  $E_s$  (Fig. 9). From the slopes of the lines the  $\delta$ 's are obtained (see Table 13). No consideration has been given to the nitro and fluoro derivatives. The values of  $\delta$  show that the reactions corresponding to the constants  $k_1$  and  $k_3$  are strongly influenced by steric effects, whereas the reverse reactions, *e.g.* those corresponding to  $k_2$  and  $k_4$  are practically independent of such effects.

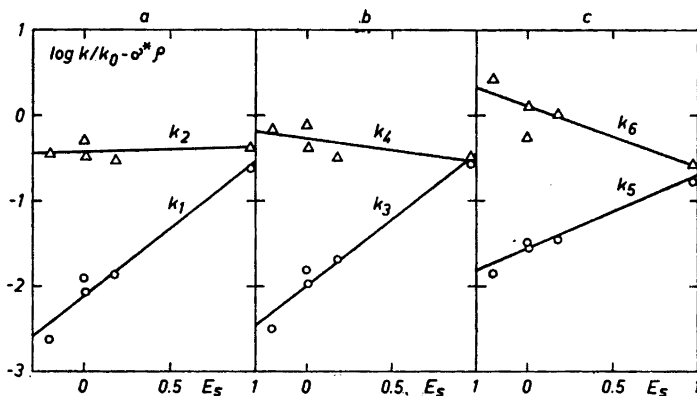


Fig. 9.  $\log k/k_0 - \sigma^* \rho$  as functions of  $E_s$ , concerning a)  $k_1$  and  $k_2$ , b)  $k_3$  and  $k_4$ , c)  $k_5$  and  $k_6$ .

#### DISCUSSION

The values of  $\rho$  and  $\delta$  which have been obtained for the six slow reactions (Scheme 1), show that the reaction mechanisms corresponding to  $k_1$  and  $k_3$  are fairly similar but are different from that corresponding to  $k_5$ . Likewise for the reverse reactions: those corresponding to  $k_2$  and  $k_4$  are similar and differ from the one corresponding to  $k_6$ . Consequently the reactions dominating in alkaline solutions occur according to other mechanisms than those dominating in neutral and acid solutions.

From the result of the above-mentioned investigations the following conclusions can be drawn concerning the mechanisms of the different reactions.

The reactions, corresponding to the constants  $k_1$  and  $k_3$ , in which the coloured forms of the dye are transformed to colourless species, are each composed of two steps. A rate-determining bimolecular reaction of the carbonium ion with a water molecule, in which the water molecule becomes bonded to the central carbon atom, followed by a rapid equilibrium between the intermediate and the colourless final product. Such rapid equilibrium could be achieved either by an internal proton transfer in which a proton from the  $\text{OH}_2^+$  group moves to one of the amino groups, or by an external one *via*  $\text{H}_2\text{O}$  or some base in the buffer system. The values of  $\rho$  obtained for these reactions are very low, which means that the influence of substituents in the *meta* or *para* positions are slight. In the case of the *ortho* derivatives it is these reactions, which are influenced by the steric hindrance. The values of the constants  $k_1$  and  $k_3$  for the *ortho* derivatives are on the average only 1% of the values of the corresponding constants for the *meta* derivatives.

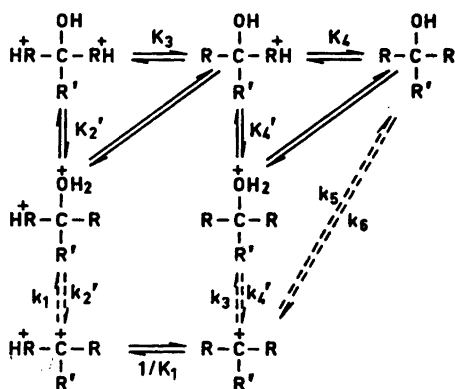
The reverse reactions, corresponding to the constants  $k_2$  and  $k_4$ , appear in the reverse order, *viz.* prior equilibrium between the stable colourless species and the intermediates, followed by a rate-determining unimolecular decompositions of these. From the large negative values of  $\rho$ , about the same values for both of the reactions, the following can be concluded:

- a) The influence of *meta* and *para* substituents is large. The electron density at the central carbon atom is largely influenced by such substituents.
- b) The reactions will be promoted by electron donating substituents, either because they facilitate the unimolecular splitting-off the water molecule, or because they cause the equilibrium between colourless species and intermediate to be displaced in the direction of the intermediate, or because both of these processes occur simultaneously.
- c) The reactions occur at the methane carbon atom and by the same mechanisms. These reactions will not be appreciably influenced by steric effects. The constants  $k_2$  and  $k_4$  are of the same magnitude for both the *ortho* and the *meta* derivatives.

The above-mentioned reactions occur in acid and neutral media. In alkaline solutions the bimolecular reaction between  $\text{OH}^-$  and the dyestuff is the dominating one. The constant  $\rho$  of this reaction has a relatively large positive value, *e.g.* the reaction is promoted by electron attracting substituents, by diminishing the electron density at the central carbon atom. Large *ortho* effects are in accordance with a bimolecular reaction.

The reverse reaction is promoted by electron donating substituents and is not influenced by steric hindrance.

The reactions can be summarized (Scheme 2):



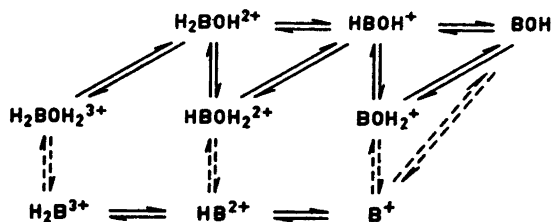
Scheme 2

The reported constants  $k_2$  and  $k_4$  are thus the product of a rate constant and an equilibrium constant:

$$k_2 = k_2' K_2'$$

$$k_4 = k_4' K_4'$$

In strongly acid solutions (concentrated sulphuric acid) a carbonium ion with three positive charges can be formed,<sup>6,21,22,23</sup> and in such solutions there is probably another way in which the reaction could occur. If the blue carbonium ion is represented by  $\text{B}^+$ , the following reaction scheme can be written (Scheme 3):



Scheme 3

Compare with Refs. 6, 10, and 27.

Rumpf and Anthony-Barbier<sup>22</sup> have proposed a similar scheme, in which, however, the direct reaction  $B^+ + OH^- \rightleftharpoons BOH$  is absent, while Ginzburg *et al.*<sup>23,24,25,26</sup> have assumed a scheme with  $HB^{2+} + OH^- \rightleftharpoons HBOH^+$  as the rate-determining reaction. However, none of these workers reported any results for kinetic investigations.

In connexion with the results of Ginzburg *et al.* several objections can be raised. Firstly, the measurements were not performed at any definite temperature; the reported value of  $18 \pm 2^\circ C$ , clearly indicates that no attention was paid to temperature control. Secondly, acetone-water mixture which was used as solvent did not have the same composition throughout all the measurements. It can be seen that the concentration of acetone varies between 0.4 % and 8 %. Thirdly, it is obvious that extinction values have been measured, which in certain cases have exceeded the value 2. At these high extinctions, the validity of the Lambert-Beers' law is questionable. Fourthly, they have assumed that for equilibrium at  $pH \sim 4$  all the dye should be in the form of the coloured ion, B. This is approximately so for some of the *ortho* derivatives, but it is not true for most of the other dyestuffs. Considering *m*-NO<sub>2</sub>-MG and *p*-NO<sub>2</sub>-MG, for instance, the concentration of coloured ion at pH 4 is only about 75 % of the total dyestuff concentration. Therefore such an assumption at pH 4 for these two dyestuffs would influence the values of their constants  $K_0$  by a factor of 2. Fifthly, in connexion with the determination of the constant  $K_C$ , they have also assumed, that the dye should consist of only B and S'' in the pH range where the measurements have been performed (pH 2.2–3.0). This, too, is erroneous since the concentrations of B + S'' vary between 90 and 98 %, depending on the dye and the pH. Because of these invalid assumptions, the results obtained by Ginzburg *et al.* are questionable!

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