# Complex Formation between Borate Ions and *o*-Hydroxy Malachite Green. An Investigation of Equilibria and Reaction Rates

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*o*-Hydroxy Malachite Green (MG) reacts with borate ions giving complexes analogous to the borate complexes of mannitol and other polyols and diols. Two complexes have been found with the probable structures I and II
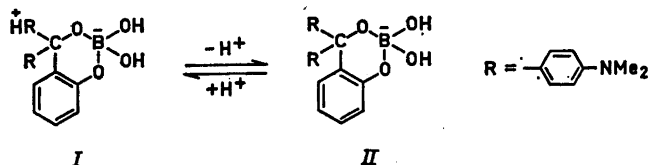


The stability constants of the complexes were determined and found to be $4.0 \times 10^3$ $M^{-1}$ for Complex I and $2.4 \times 10^4$ $M^{-1}$ for Complex II. The protolytic constant for [Complex II] [$H^+$]/[Complex I] was found to be $1.6 \times 10^{-8}$ M.

The rate constants for the reactions

$$MG + borate \rightleftharpoons Complex\ I$$
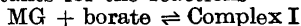
were determined to $7.5 \times 10^2$ $min^{-1}$ $M^{-1}$ for the forward reaction and 0.19 $min^{-1}$ for the backward reaction.

The measurements were carried out spectrophotometrically at 20°C and constant ionic strength 0.5 M

In alkaline solutions borate ions react with *o*-hydroxy Malachite Green (MG) in a manner similar to that in which borate ions react with mannitol, pyrocatechol and other polyols or diols. *o*-Hydroxy Malachite Green behaves like a diol in borate solutions. An aqueous solution of MG is rapidly decoloured when it is mixed with a borate buffer owing to complex formation.

o-Hydroxy MG



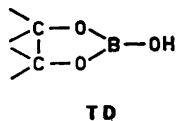(colourless)                              (coloured)
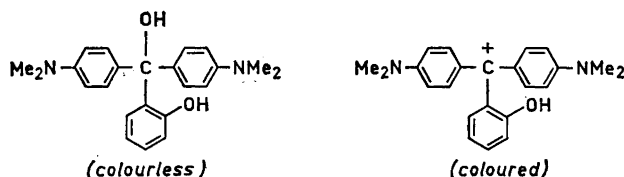
Previous investigations of the complex formation between borate ions and diols show that the following types of complexes are formed [1-7] (**D** = diol, **T** = borate)



TD⁻                      and                      TD₂⁻
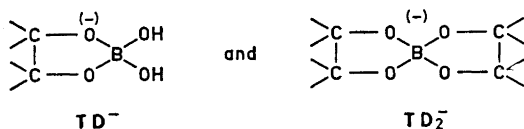
It has also been found that neutral complexes can be formed. Böeseken and Niks (Ref.[2]) suppose that the neutral complex is of the following type
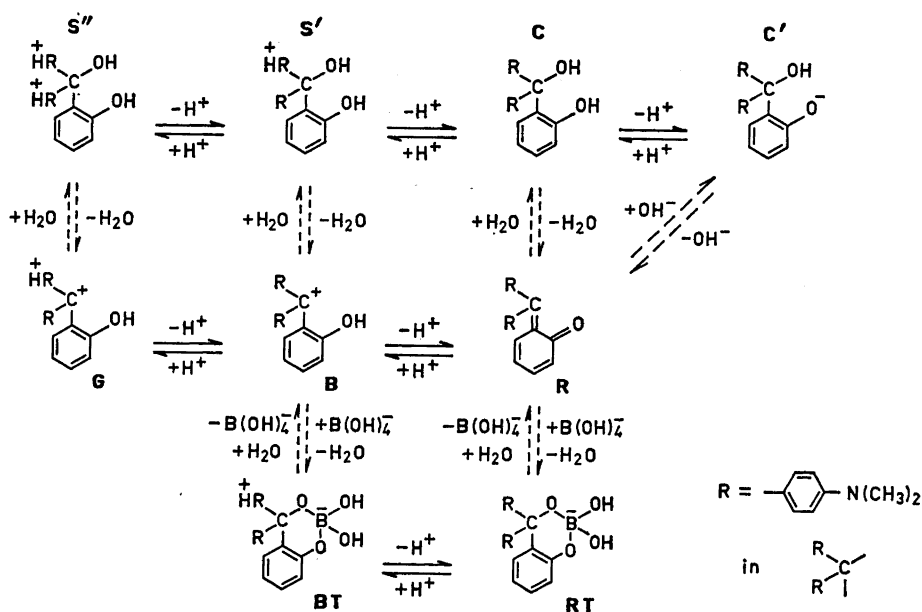


TD

Complexes of the type $TD_2$ have not been found, however.

The purpose of this investigation is to determine stability constants and reaction rate constants for the complex formation between borate ions and MG.

In weakly alkaline aqueous solutions of MG the dye is present in the form of two coloured and three colourless species. In acid solutions there are two additional forms, one coloured and one colourless. The complicated equilibrium scheme has been analyzed by the author in a previous paper [8]. If borate buffers are used the equilibrium scheme is complicated further by the formation of one or more borate complexes. The investigations carried out now show that two borate complexes are formed which, however, do not exactly correspond to the types of complexes shown above since MG gives six-membered-rings and not the usual five-membered-rings. Complexes with two diols per borate have not been found, a fact that is not surprising since the total concentration of the due stuff was kept as low as $10^{-5}$ M. Higher concentrations of the dye cannot be used since the preparation of the dye used was the very slightly soluble perchlorate which can be obtained in a very pure state. Further, one of the carbinol forms of the dye is almost insoluble and will precipitate in a certain pH-range if higher concentrations of the dye are used.

The following equilibrium scheme indicates schematically the reactions that can take place if the pH of a solution of MG is changed and borate buffers are used in addition to other buffers:
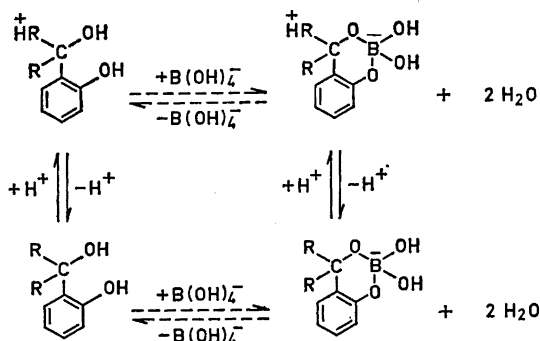
Scheme I

S″   S′   C   C′

HR  OH    HR  OH    R  OH    R  OH
HR  C          R  C          R  C          R  C
    OH           OH           OH           O⁻

$-H^+$ ⇌ $+H^+$   $-H^+$ ⇌ $+H^+$   $-H^+$ ⇌ $+H^+$

$+H_2O$ ⇌ $-H_2O$   $+H_2O$ ⇌ $-H_2O$   $+H_2O$ ⇌ $-H_2O$   $+OH^-$ ⇌ $-OH^-$

HR  C⁺    R  C⁺    R  C
R       OH   R   OH   R   O

G   B   R

$-H^+$ ⇌ $+H^+$   $-H^+$ ⇌ $+H^+$

$-B(OH)_4^-$ ⇌ $+B(OH)_4^-$   $-B(OH)_4^-$ ⇌ $+B(OH)_4^-$
$+H_2O$ ⇌ $-H_2O$   $+H_2O$ ⇌ $-H_2O$

HR  O  OH    R  O  OH
R  C  B      R  C  B
   O   OH       O   OH

BT   $-H^+$ ⇌ $+H^+$   RT

$R = $ ⟨benzene ring⟩ $-N(CH_3)_2$

in   $\begin{matrix} R \\ R \end{matrix} \overset{}{C}$

Whole arrows indicate that the reactions proceed with a non-measurable velocity — that is, instantaneously — whereas dashed arrows indicate that the reactions take place with a measurable velocity.

It would seem probable that the borate ions should react with the hydrated forms of the dye, S′ and C, which are diols, and not with the coloured dehydrated forms, B and R. The same complexes can be formed irrespective of the borate ions reacting with the hydrated forms (Scheme II) or with the dehydrated forms (Scheme I). However, kinetic measurements support the reactions according to Scheme I.

Scheme II

HR  OH         HR  O  OH
R  C            R  C  B      + 2 H₂O
   OH              O   OH

$+B(OH)_4^-$ ⇌ $-B(OH)_4^-$

$+H^+$ ⇅ $-H^+$          $+H^+$ ⇅ $-H^+$

R  OH          R  O  OH
R  C            R  C  B      + 2 H₂O
   OH              O   OH

$+B(OH)_4^-$ ⇌ $-B(OH)_4^-$

One cannot conclude from the measurements whether the neutral complex has the structure



$$I \qquad\qquad\qquad II$$

The latter structure was suggested by Hermans [1] for neutral complexes between borate ions and diols. Compounds of type II with three-coordinated boron have proved to be very weak acids, weaker than boric acid (Hermans [1]). The present investigations show, however, that the complex BT is a considerably stronger acid than boric acid. Therefore, is seems likely that the proton released is bound to a nitrogen in an amino group and not to the oxygen in the group B—OH. This speaks for the structure I. There are, however, no absolutely sure proofs of boron having a four-coordinated configuration (Structure I) or a three-coordinated configuration (Structure II) in complexes between borate ions and polyols.

## DEDUCTION OF SOME EQUATIONS USED

The same symbols and definitions have been used as in Ref.[8] Further, the following symbols are defined:

$C_T$ = total concentration of boron

[T] = the concentration of the borate ions which are assumed to be present only as the species $B(OH)_4^-$

$$K_{BT} = \frac{[BT]_\infty}{[B]_\infty[T]_\infty} \quad ; \quad K_{RT} = \frac{[RT]_\infty}{[R]_\infty[T]_\infty} \quad ; \quad K = \frac{[RT][H^+]}{BT]}$$

$k_3'$ = rate constant for the reaction B + T → BT
$k_4'$ = » » » » » BT → B + T
$k_5'$ = » » » » » R + T → RT
$k_6'$ = » » » » » RT → R + T

## A. Equilibrium measurements

The stability constants $K_{BT}$ and $K_{RT}$ were determined by light absorption measurements on solutions of o-hydroxy Malachite Green in different borate buffers when equilibrium was reached. The measurements were carried out at the wave length 6090 Å where B and R proved to be the only species in the solutions that absorb light.

In weakly alkaline solutions where the concentrations of the yellow form, G, and its hydrated form, S″, can be omitted in comparison to the concentrations of the other forms of the dye, the following equations are obtained:

$$C_M = [\text{B}]_\infty + [\text{R}]_\infty + [\text{BT}]_\infty + [\text{RT}]_\infty + [\text{S}']_\infty + [\text{C}]_\infty + [\text{C}']_\infty \qquad (1)$$

According to the definitions of the constants eqn. (1) can be written

$$C_M = [\text{B}]_\infty \left[ 1 + \frac{K_7}{\text{h}} + [\text{T}]K_{\text{BT}} + \frac{K_7}{\text{h}}[\text{T}]K_{\text{RT}} + \frac{1}{K_6}\left(1 + \frac{K_4}{\text{h}} + \frac{K_4 K_8}{\text{h}^2}\right) \right] (2)$$

The absorbancy per cm, $e_\infty$, in a solution is

$$e_\infty = \varepsilon_{\text{B}}[\text{B}]_\infty + \varepsilon_{\text{R}}[\text{R}]_\infty = \frac{[\text{B}]_\infty}{C_M}\left(e_{\text{B}} + e_{\text{R}}\frac{K_7}{\text{h}}\right) \qquad (3)$$

A combination of eqns. (2) and (3) gives, since $e_{\text{B}} = C_M \varepsilon_{\text{B}}$ and $\varepsilon_{\text{R}} = C_M \varepsilon_{\text{R}}$,

$$\left(K_{\text{BT}} + \frac{K_7}{\text{h}}K_{\text{RT}}\right)[\text{T}] = \frac{e_{\text{B}} + e_{\text{R}}K_7/\text{h}}{e_\infty} - 1 - \frac{K_7}{\text{h}} - \frac{1}{K_6}\left(1 + \frac{K_4}{\text{h}} + \frac{K_4 K_8}{\text{h}^2}\right) (4)$$

In eqn. (4) the terms [T], $e_\infty$, and h can be measured. The terms $K_7$, $e_{\text{B}}$, $e_{\text{R}}$, $K_6$, $K_4$, and $K_8$ are known from earlier investigations (Ref.[8]). Thus the constants $K_{\text{BT}}$ and $K_{\text{RT}}$ can be determined if the measurements can be carried out in a sufficiently large pH-range.

## B. Kinetic measurements

In Ref.[8] there is an equation (eqn. 7) for the total rate constant of the protolytic reactions shown in the equilibrium scheme which is applicable to MG. If we wish to extend this eqn. (7) to include the complex formation with borate ions too, considerable difficulties arise. In kinetic measurements only the colour change, which occurs when the coloured species are transformed to colourless carbinol species and borate complexes, can be followed. An approximate method of determining at least some of the rate constants for the complex formation has been tried based on the following facts: (1) When a solution of MG, containing the dye only in the form of the species B and R, is mixed with a borate buffer the solution fades to about 3—10 % at pH = 8 and 0.3—1 % at pH = 9 of the initial colour intensity. The fading increases when $[\text{B(OH)}_4^-]$ increases. (2) The total reaction runs as a first-order reaction, with reasonable accuracy, if the reaction is followed only until 50—75 % of the dye has reacted. Since the total concentration of the dye, $C_M$, is $\ll [\text{B(OH)}_4^-]$ and the measurements are carried out in buffer solutions all reaction steps become pseudomonomolecular. The total reaction deviates from a first-order reaction only in solutions with low pH and high $C_T$. (3) Since the equilibrium "coloured" $\rightleftharpoons$ "colourless" is strongly displaced towards the right the contribution to the total reaction rate from the reactions BT $\xrightarrow{k_4'}$ B + T and RT $\xrightarrow{k_6'}$ R + T probably can be omitted when only B and R are present at the start of the reactions and nothing of BT or RT.

If $k_4'$ and $k_6' \ll k_3'$ and $k_5'$ the following equations can be deduced:

$$\frac{\text{d}}{\text{d}t}([\text{R}] + [\text{B}] + [\text{G}]) = k_2[\text{S}''] + k_4[\text{S}'] + k_6[\text{C}] + k_8[\text{C}'] - k_1[\text{G}] - k_3[\text{B}] - k_5[\text{R}] - k_3'[\text{B}][\text{T}] - k_5'[\text{R}][\text{T}] - k_7[\text{R}]\text{oh} \qquad (5)$$

Eqn. (5) is written

$$U\frac{d[R]}{dt} = Q[S''] - P[R] \quad \text{where} \tag{6}$$

$$U = 1 + h/K_7 + h^2 K_1/K_7 \tag{7}$$

$$Q = k_2 + k_4 K_3/h + k_6 K_3 K_4/h^2 + k_8 K_3 K_4 K_8/h^3 \tag{8}$$

$$P = k_1 h^2 K_1/K_7 + k_3 h/K_7 + k_5 + k_7 oh + k_3'[T]h/K_7 + k_5'[T] \tag{9}$$

It further holds that

$$C_M = [R] + [B] + [G] + [S''] + [S'] + [C] + [C'] + [BT] + [RT] \tag{10}$$

which can be written

$$C_M = [R]M + [S'']N \quad \text{where} \tag{11}$$

$$M = 1 + h/K_7 + h^2 K_1/K_7 + [BT]/[R] + [RT]/[R] \tag{12}$$

$$N = 1 + K_3/h + K_3 K_4/h^2 + K_3 K_4 K_8/h^3 \tag{13}$$

Eqn. (6) can now be transformed to

$$\frac{d[R]}{dt} = \frac{QM + PN}{UN}\left(\frac{QC_M^-}{QM + PN} - [R]\right) = k(a - [R]) \tag{14}$$

Integration gives if M is constant (*cf.* Cigén [9], p. 1463)

$$k = \frac{1}{t}\ln\frac{[R]_\infty - [R]_0}{[R]_\infty - [R]_t} = \frac{1}{t}\ln\frac{e_0 - e_\infty}{e_0 - e_t} \tag{15}$$

The rate constant, $k$, can be written

$$k = \frac{Q}{N}\left(1 + \frac{[BT] + [RT]}{U[R]} + \frac{V}{U} + \frac{k_3'[T]h/K_7 + k_5'[T])}{U}\right) \tag{16}$$

where

$$V = P - k_3'[T]h/K_7 - k_5'[T] \tag{17}$$

The terms $Q/N + V/U$ are the same as $k$ in eqn. (7) in Ref.[8] and eqn. (26) in Ref.[9] The values of $Q/N + V/U$ at different pH-values are obtained from measurements in borate free solutions. However, $k$ in eqn. (16) becomes approximately constant only if the term $\dfrac{Q([BT] + [RT])}{NU[R]}$ is small in comparison with the other terms in eqn. (16). If this is true and if $(k_3'[T]h/K_7 + k_5'[T])/U \gtrsim Q/N + V/U$ the rate constant $k'_3$ and (or) $k_5'$ can be determined. Then the rate constant $k_4'$ and (or) $k_6'$ can be calculated from the equations

$$k_4' = k_3'/K_{BT} \tag{18}$$

$$k_6' = k_5'/K_{RT} \tag{19}$$

## EXPERIMENTAL

*Chemicals used.* o-Hydroxy Malachite Green was prepared in the form of the per-chlorate. The same preparation was used as in Ref.[8] Boric acid, potassium chloride, sodium hydroxide, all of analytical grade, were used in the buffer solutions. Potassium chloride was used to keep the ionic strength constant (0.5 M).

A stock solution of the dye was prepared by shaking a weighed sample of the MG perchlorate for 20 h with a 0.5 M potassium chloride solution which was heated to 70°C before the shaking was started. The volume of the solution was adjusted to the desired one at a temperature of 20°C, and the stock solution was allowed to stand for four days. The concentration of the dye in the stock solution, $C_M$, was determined spectrophoto-metrically; $C_M = 1.02 \times 10^{-5}$ M. The weighed sample of MG was calculated to give $C_M = 1.05 \times 10^{-5}$ M. The difference is due partly to the absorption of dyestuff on the walls of the glass flask used and perhaps partly to the fact that some of the very slightly soluble MG perchlorate may have remained undissolved. The method previously used (Ref.[8]) to prepare a stock solution by dissolving the MG perchlorate in acetone which is then diluted with a potassium chloride solution, was not employed in this investiga-tion in order to avoid the possibility of disturbances in the measurements from the acetone.

The borate buffers were prepared from carbon dioxide free solutions of sodium hyd-roxide, boric acid, and potassium chloride; ionic strength 0.5 M. A solution for measure-ment was obtained by mixing equal volumes of a borate buffer and a dye stock solution. The pH of the solutions for measurement was determined by emf. measurements at 20.0°C on elements of the following type

$$
\text{H}_2, \text{Pt} \left| \begin{array}{l} \text{10 mM HCl} \\ \text{490 mM KCl} \\ \text{quinhydrone} \end{array} \right| \begin{array}{c} \text{conc.} \\ \text{KCl} \end{array} \left| \begin{array}{l} \text{Borate} \\ \text{buffer} \end{array} \right| \text{Pt, H}_2
$$

pH means $-\log[\text{H}^+]$ and not $-\log a_{\text{H}+}$.

Three series of measurements were carried out with different total concentration of boric acid; $C_T = 25$, $12.5$, and $6.25$ mM. The pH-range used was pH $= 8 - 9.7$. The concentration of the borate ions, [T], varied in the three series between $3 - 22$ mM, $1.5 - 11$ mM, and $0.75 - 5.5$ mM. Further it was assumed that no polyborate ions need to be considered at these comparatively low concentrations of boric acid. According to Ingri *et al.*[10] it can be assumed that the greatest part of the boric acid is present as monomer acid and monomer borate ion when $C_T \leq 25$ mM. However, the polyborate formation is strongest at pH-values $\approx pK_s$ of the boric acid, *i.e.* at pH $= 9$, and it is possible that a certain polyborate formation occurs in the series of measurements with $C_T = 25$ mM.

*Apparatus.* The equilibrium and kinetic measurements were carried out spectrophoto-metrically with a Beckman quartz spectrophotometer with photo multiplier. The spectro-photometer was furnished with the arrangements for rapid kinetic studies described in Ref.[8] when the kinetic measurements were carried out.

## RESULTS

*Equilibrium measurements.* In three series of measurements at seven different pH-values in each series the equilibrium absorbancy, $E_\infty$, of the solutions, obtained by mixing equal volumes of borate buffer and dye stock solution, was read. The measurements were carried out at the wavelength $\lambda = 609$ m$\mu$ where the coloured species R has an absorption maximum. At this wavelength it also happens that $\varepsilon_R = \varepsilon_B$. Absorption cells of quartz, optical length $= 5$ cm, were used. The recorded absorbancies were very low but reproducible for the highest borate concentrations. Table 1 contains the corresponding values of $E_\infty$, pH and $C_T$ and the values of $K_{RT}$ and $K_{BT}$ calcu-lated from eqn. (4).

*Table 1.* Determination of $K_{BT}$ from eqn. (4). $K_{RT}$ is taken $= 6 K_{BT}$. $C_M = 0.5 \times 10^{-5}$ M. $\lambda = 609$ m$\mu$. $T = 20.0°C$. $d = 5$ cm. $e_B = e_R = 0.420$.

| $C_T = 25$ mM | | | | $C_T = 21.5$ mM | | | | $C_T = 6.25$ mM | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | [T] mM | $E_\infty = 5 e_\infty$ | $K_{BT} \times 10^{-2}$ | pH | [T] mM | $E_\infty = 5 e_\infty$ | $K_{BT} \times 10^{-2}$ | pH | [T] mM | $E_\infty = 5 e_\infty$ | $K_{BT} \times 10^{-2}$ |
| 8.04 | 3.0 | 0.085 | 35 | 8.04 | 1.50 | 0.145 | 37 | 8.02 | 0.75 | 0.256 | 36 |
| 8.25 | 4.5 | 0.045 | 37 | 8.25 | 2.25 | $0.080_5$ | 39 | 8.24 | 1.125 | 0.139 | 41 |
| 8.42 | 6.0 | 0.028 | 39 | 8.42 | 3.00 | $0.049_5$ | 42 | 8.40 | 1.50 | 0.091 | 42 |
| 8.56 | 7.5 | 0.021 | 37 | 8.56 | 3.75 | 0.036 | 41 | 8.55 | 1.875 | 0.065 | 42 |
| 8.69 | 9.0 | $0.015_5$ | 38 | 8.68 | 4.50 | $0.027_5$ | 41 | 8.67 | 2.25 | 0.053 | 40 |
| 8.95 | 12.5 | $0.010_5$ | 34 | 8.93 | 6.25 | 0.018 | 39 | 8.92 | 3.125 | 0.033 | 40 |
| 9.19 | 16.0 | 0.008 | 32 | 9.17 | 8.00 | 0.014 | 35 | 9.15 | 4.00 | 0.024 | 39 |
| Mean values | | | 36 | | | | 39 | | | | 40 |

The measurements cannot be carried out within a wider pH-range than pH $= 8-9.2$ and this is why the constants $K_{RT}$ and $K_{BT}$ cannot be determined separately. By trial and error it was found that the best constancy for $K_{RT}$ and $K_{BT}$ was obtained if $K_{RT}$ was taken $= 6\ K_{BT}$.

From Table 1 it can be seen that the mean value of $K_{BT}$ decreases by 10 % when $C_T$ is increased from 6.25 mM to 25 mM. On the other hand the differences between the $K_{BT}$-values at $C_T = 6.25$ mM and 12.5 mM are not significant. A possible formation of polyborate would give too low values of $K_{BT}$. Therefore the value $K_{BT} = 4.0 \times 10^3$ M$^{-1}$ must be considered as most reliable. This gives $K_{RT} = 2.4 \times 10^4$ M$^{-1}$.

By definitions $K = K_{BT}K_7/K_{RT}$. From Ref.[8] we get $K_7 = 2.72 \times 10^{-9}$ M and this gives $K = 1.6 \times 10^{-8}$ M$^{-1}$.

In calculating $K_{BT}$ from eqn. (4) the values of $K_7$, $K_6$, $K_4$, and $K_8$ were used which had been obtained in a previous investigation on o-hydroxy Malachite Green (Ref.[8]). The solutions used in these previous measurements contained 2 % of acetone which, of course, might have influenced the values of the constants determined. However, the influence on the values of $K_{BT}$ and $K_{RT}$ from the above-mentioned small errors that eventually exist in the constants is insignificant. The values of $e_B$ and $e_R$ were determined in solutions free from acetone by the same methods as those used in Ref.[8]

*Kinetic measurements.* Three series of kinetic measurements, corresponding to the equilibrium measurements but partly at different pH-values, were carried out; Table 2. Furthermore, $Q/N + V/U$ in eqn. (16) (corresponding to $k$ in eqn. (7), Ref.[8]) was determined by kinetic measurements in buffer solutions free from acetone and borate. An attempt to calculate both $k_3'$ and $k_5'$ showed that $k_3' \gg k_5'$ and therefore $k_5'$ cannot be calculated from eqn. (16).

The rate constant $k_3'$ was calculated in the following way. Equal volumes of a borate buffer and a dye stock solution are mixed. In the stock solution all of the dye is present as the coloured ion B, $C_M = [B]$. The equilibrium $B \rightleftharpoons H^+ + R$ is reached instantaneously and the solution is decolourized owing to the formation of the colourless species S', C, C', BT, and RT. The reactions are followed at low pH until $[B] + [R] \approx \frac{1}{2} C_M$ and at high pH until $[B] + [R] \approx \frac{1}{4} C_M$. The total rate constant $k$ in eqn. (16) is then determined since the term $\dfrac{Q}{N} \cdot \dfrac{[BT] + [RT]}{U[R]}$ in eqn. (16) is so small that it can be omitted in comparison with the other terms in eqn. (16). This can be done without large errors since $Q/N$ only amounts to between 1.5 and 14 % of $k$ (see Table 2) and $\dfrac{[BT] + [RT]}{U[R]} < \frac{1}{4}$ when 50 % of the dye has reacted. Therefore the rate constant $k_3'$ can be calculated from the approximate equation

$$k_3' = \frac{(k-Q/N-V/U)U}{[T]h/K_7} \tag{20}$$

Table 2 shows that $k_3'$ decreases when pH increases which is in qualitative agreement with the approximations undertaken. The series of measurements with $C_T = 25$ mM shows, however, that the approximations introduced cannot

*Table 2.* Determination of $k_3'$ from eqn. (20). $C_M = 1 \times 10^{-5}$ M, $\lambda = 609$ m$\mu$, $T = 20.0°$C.

| pH | $Q/N + V/U$ min$^{-1}$ | $Q/N$ min$^{-1}$ | $C_T = 25$ mM | | $C_T = 12.5$ mM | | $C_T = 6.25$ mM | |
|---|---|---|---|---|---|---|---|---|
| | | | $k$ min$^{-1}$ | $k_3'$ min$^{-1}$ M$^{-1}$ | $k$ min$^{-1}$ | $k_3'$ min$^{-1}$ M$^{-1}$ | $k$ min$^{-1}$ | $k_3'$ min$^{-1}$ M$^{-1}$ |
| 8.04 | 0.309 | 0.106 | 2.16 | 804 | 1.23 | 795 | 0.765 | 790 |
| 8.42 | 0.415 | 0.097 | 3.13 | 774 | 1.75 | 758 | 1.105 | 785 |
| 8.68 | 0.507 | 0.088 | 3.40 | 737 | 1.98 | 751 | 1.23 | 742 |
| 8.93 | 0.564 | 0.074 | 3.36 | 739 | 1.98 | 744 | 1.29 | 765 |
| 9.17 | 0.615 | 0.060 | 2.83 | 693 | 1.72 | 693 | 1.225 | 762 |
| 9.42 | 0.631 | 0.044 | 2.28 | 705 | 1.48 | 721 | 1.09 | 781 |
| 9.72 | 0.652 | 0.025 | 1.63 | 679 | 1.16 | 709 | 0.93 | 762 |
| Mean values | | | | 733 | | 739 | | 770 |

alone be responsible for the comparatively large differences of $k_3'$ within this series. The explanation may be that polyborate ions are formed and therefore the $k$-values obtained become too low. (*Cf.* the low values of $K_{BT}$ in the corresponding series of equilibrium measurements with $C_T = 25$ mM). As a mean of all $k_3'$-values $k_3' = 7.5 \times 10^2$ min$^{-1}$ M$^{-1}$ was obtained. Eqn. (18) gives then $k_4' = 0.19$ min$^{-1}$.

In Fig. 1 curve D gives $Q/N + V/U$ as a function of pH. In Fig. 1 is also plotted $k$ as a function of pH calculated from eqn. (20) for different $C_T$ using the mean-value $k_3' = 746$. Curve A, $C_T = 25$ mM; curve B, $C_T = 12.5$ mM; Curve C, $C_T = 6.25$ mM.

If the correction term $([BT] + [RT])/U[R]$ is introduced into eqn. (20) a better coincidence is obtained between the experimentally found points
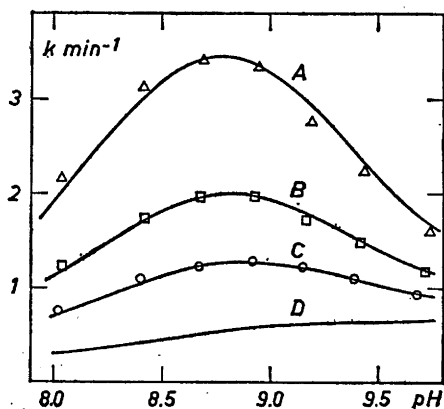


*Fig. 1.* The rate constant $k$ as a function of pH. Curve A, $C_T = 25$ mM; Curve B, $C_T = 12.5$ mM; Curve C, $C_T = 6.25$ mM. The full drawn curves are calculated from eqn. (20). The symbols are experimentally found $k$-values. Curve D shows the experimentally found values of $Q/N + V/U$, *i.e.* the rate constant of the total reaction in solutions free from borate, as a function of pH.

($\triangle$, $\square$, and $\bigcirc$) and the full drawn calculated curves B and C as well as the left part of curve A. The correction has not been carried out because experimental errors and a possible polyborate formation give an uncertainty of the rate constant $k_3'$ greater than the correction term, except at the lowest pH.

## DISCUSSION

In an aqueous solution of o-Hydroxy Malachite Green with pH = 5—6 the dye is present as the coloured species B and R. If such a solution is made weakly alkaline with a suitable buffer the solution is decoloured. However, the fading proceeds about ten times faster at pH = 8—9 in borate buffers than in ammonia-ammonium chloride buffers. This high reaction rate in borate buffers shows that the borate complexes are formed by the reactions B + T → BT and R + T → RT indicated in Scheme I. If the borate complexes were formed according to the reactions indicated in Scheme II the rate of the decolourization should be of the same magnitude as in borate free buffers since the slow reactions B + $H_2O$ → S' and R + $H_2O$ → C must precede the complex formation S' + T → BT + $H_2O$ and C + T → RT + $H_2O$.

The kinetic measurements show that the rate of the complex formation is directly proportional to the concentration of the positively charged coloured ion B and to the concentration of the borate ions and that the rate constant $k_3' \gg k_5'$. The complex RT which is considerably stronger than the complex BT is thus formed mainly by the fast reaction BT → RT + $H^+$ and not by the slow reaction R + T → RT.

## REFERENCES

1. Hermans, P. H. Z. anorg. u. allgem. Chem. 142 (1924) 83.
2. Böeseken, J. and Niks, A. Rec. trav. chim. 59 (1940) 1062.
3. Schäfer, H. Z. anorg. u. allgem. Chem. 247 (1941) 96.
4. Böeseken, J. Advances in Carbohydrate Chem. 4 (1949) 189.
5. Deutsch, A. and Osoling, S. J. Am. Chem. Soc. 71 (1949) 1637.
6. Ross, S. D. and Catotti, A. J. J. Am. Chem. Soc. 71 (1949) 3563.
7. Torssell, K. Arkiv Kemi 3 (1952) 571.
8. Cigén, R. Acta Chem. Scand. 16 (1962) 192.
9. Cigén, R. Acta Chem. Scand. 12 (1958) 1456.
10. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. Acta Chem. Scand. 11 (1957) 1034.