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EQUILIBRIUM AND KINETIC STUDIES ON BRILLIANT GREEN

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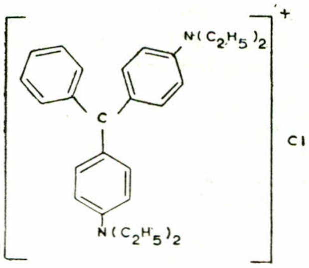
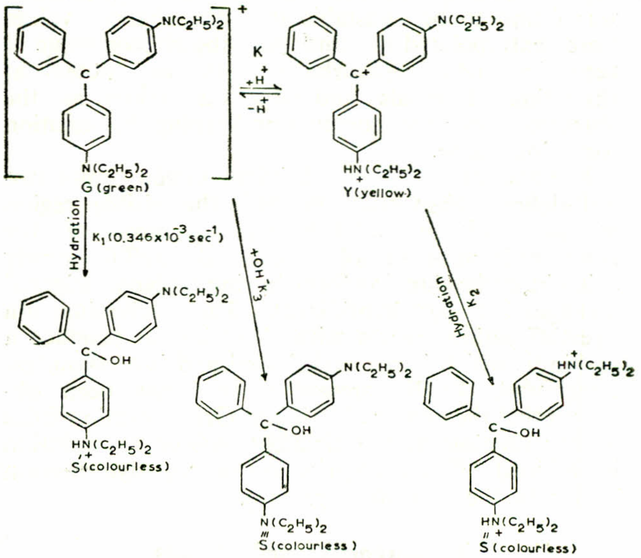
Abstract. A neutral aqueous solution of Brilliant Green is of intense green colour. The solution is slowly decolorized as the dye cation is changed to a colourless species due to hydration. The rate constant for the hydration step is $k_I=0.354\times10^{-3}$ sec. On adding hydrochloric acid solution to a freshly prepared Brilliant Green solution, it turns yellow as the Brilliant Green cation is protonated. The equilibrium between green and yellow species is established instantaneously. The equilibrium constant K for the protonation of the dye cation is found to be $140.5/M$. The yellow species is unstable in acidic solution and it is hydrated at a faster rate to produce a colourless species. The rate constant determined with varying concentrations of the acid, lies in the range 4.62×10^{-3} sec to 5.88×10^{-3} sec. The rate of decolorization in this step is about 13–16 times faster than in the neutral solution. The rate constant k_3 for decolorization of Brilliant Green in sodium hydroxide is found to be 29–37 times faster than the decolorizing rate in neutral aqueous medium. The measurements for the equilibrium constant and the three rate constants were made spectrophotometrically.

The salt-like, triphenyl carbonium ion dyestuffs, are intensely bright coloured compounds which are not fast to light and are thus unsuitable for many purposes, but are still valuable for certain styles of textile printing. In recent years, these basic dyes have gained much importance for being used as fast colouring materials when mixed with synthetic fibres and plastics in the molten state. Therefore, the study of properties of this class of compounds has attracted the attention of various investigators. Malachite green[1,2] and a number of its analogous derivatives[3] have been extensively investigated for the protolytic equilibria and reaction kinetics has been investigated in aqueous solutions. The present investigation is related to the protolytic and hydration reactions of Brilliant Green in aqueous and methanol dioxane solutions. Brilliant Green (I) is an unsymmetrical molecule where one of the auxochromes is removed.



I

On adding acid to a freshly prepared Brilliant Green solution, the green colour is immediately changed to yellow and then it is partially decolorized owing to hydration reactions. If the green solution is made alkaline, it is completely decolorised at a rate that is directly proportional to [OH⁻].
These reactions can be visualized with the following reaction scheme.



II

The protonation reaction proceeds at an unmeasurable rate and the equilibrium $G+H^+ \rightleftharpoons Y$ is established instantaneously.

Definition of Constants and Symbols

The equilibrium constant for protonation

$$G+H^+ \rightleftharpoons Y$$
$$K=\frac{[Y]}{[G]\,[H^+]}$$

k_I, rate constant for the hydration reaction $G+H_2O \longrightarrow S'$

k_2, rate constant for the hydration reaction of the protonated species. $Y \longrightarrow S''$

k_3, rate constant for the reaction $G \longrightarrow S'''$

A_0, A_t, A_∞, absorbance/cm of a solution at times 0, t and at infinity.

A, absorbance of the Brilliant Green solution at λ_{max} when varying amount of acid was added for equilibrium constant determinations.

ε_G molar extinction coefficient of Brilliant Green.

Experimental

Purification of Brilliant Green. The dyestuff was obtained as a commercial sample. It was purified from ethanol till the molar extinction coefficient at the λ_{max} did not increase any further on repeated crystallisations. Thus complete removal of impurities was ensured.

Kinetic Measurements. The reaction rates were followed spectrophotometrically. Optical density was recorded preferably at λ_{max} absorption peak. A Unicam SP 500 spectrophotometer was used for all the measurements.

The dye solutions were prepared immediately before starting a kinetic run. As the dye solution was found to be unstable the absorbance values were extrapolated to find the absorbance value at zero time (A_0). Absorbance, A^t, as noted at short-time intervals and A_∞ was taken as the absorbance became constant on keeping the solution for a long time.

In aqueous solution, Brilliant Green shows two well-defined absorption bands in the visible region at λ_{max} =433 and λ=628 nm. In most of the reactions in aqueous solution, the dyestuff frequently exists in carbonium ion form having a planar, trigonal arrangement (sp^2 hybridized). The carbonium ion dyestuff cation reacts with OH^- ion to produce a carbinol which is sp^3 hybridized and is a colourless compound. In the present work, it has been observed that the colour of Brilliant Green solution fades away with time and ultimately colourless solution is obtained. The decolorization of the dye solution is due to the hydration process.

Measurements and Results

The spectral changes for Brilliant Green in neutral aqueous solution are shown in Fig. 1.

Determination of Equilibrium Constant K. The dye stock solution was mixed with suitable volumes of hydrochloric acid solutions with known concentration. A_0 was determined by extrapolating the absorbance to $t = 0$. The measurements were made at λ_{max} =628 nm.

Equilibrium Constant Values

$[G]_{\text{stoichiometric}} = 0.25 \times 10^{-4}$M

$[G]_{\text{Equilibrium}} = \dfrac{\text{Absorbance}}{\varepsilon_G}$

$[Y]_{\text{Equilibrium}} = [G]_{\text{stiochiometric}} - [G]_{\text{Equilibrium}}$

$[H^+]_{\text{Equilibrium}} = [H^+]_{\text{stiochiometric}} - [Y]_{\text{Equilibrium}}$

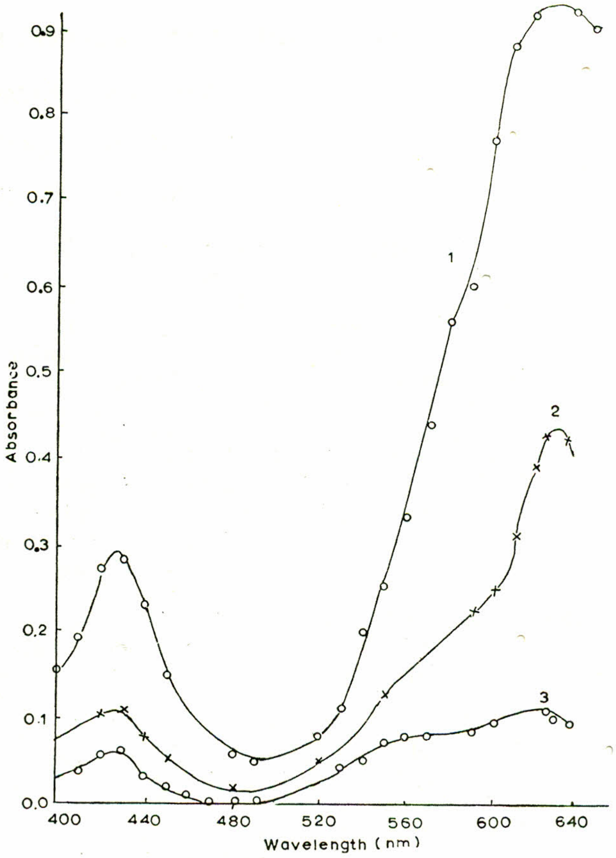


Fig. 1. Aqueous Brilliant Green solution 2×10^{-5}M. (1) just after preparation, (2) after two hours, (3) after 48 hours.

The equilibrium constant values, obtained by putting the equilibrium concentrations in equation (1), are given in Table 1.

The measurements were carried out at wavelength λ 628 nm. Let A_0 be the absorbance of neutral Brilliant Green solution. In presence of acid, while keeping the stiochiometric concentration of the dye constant, absorbance A decreases. The absorbance A_0—A corresponds to the protonated yellow species that does not absorb at 628 nm. The equilibrium constant may be written as:

$$G + H^+ \rightleftharpoons Y$$

$$K = \frac{[Y]}{[G][H^+]} \qquad \ldots\ldots\ldots(1)$$

$$\frac{[Y]}{[G]} = \frac{A_0 - A}{A - A_\infty}$$

$$K = \frac{1}{[H^+]} \cdot \frac{A_0 - A}{A - A_\infty}$$

As A_∞ value could not be reached equal to zero, hence a plot of $\dfrac{[H^+]}{A_0 - A}$ against H^+ was found to be rectilinear and K was found from the values of slope and intercept (Fig.2). A good linear plot was obtained, showing 1:1 adduct formation.

Determination of Rate Constant k_1. The rate of decolorization was followed by observing the change

TABLE 1. EQUILIBRIUM CONSTANT VALUES FOR THE PROTONATION OF BRILLIANT GREEN.

$[G]_{stoic.} \times 10^4$ (M)	$[H^+]_{stoic.} \times 10^2$ (M)	Absorbance $=628$ nm λ_{max}	$[G]_{Equilibrium}$ (M)	$[Y]_{Equilibrium}$ (M)	$[H^+]_{Equilibrium}$ (M)	$K=\frac{[Y]}{[G][H^+]}$ (M^{-1})
0.25	0.00	1.30 A_o	—	—	—	—
,,	1.00	0.50 A_t	0.096	0.154	0.00998	151
,,	2.00	0.37	0.171	0.179	0.0198	136
,,	3.00	0.25	0.048	0.202	0.0299	140
,,	4.00	0.20	0.038	0.212	0.0399	140
,,	5.00	0.17	0.032	0.218	0.0499	136
,,	6.00	0.14	0.027	0.223	0.0599	140

Mean $K = 140.5\ M^{-1}$

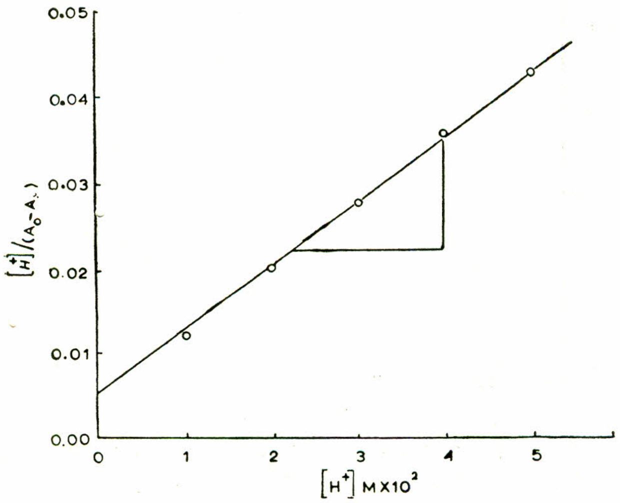


Fig. 2. Plot of $\frac{[H^+]}{A_o-A}$ versus $[H^+]$

in optical density at $\lambda_{max} = 628$ nm. The A_o values were obtained by extrapolation method. The average rate-constant for the hydration reaction k_I was found to be 0.346×10^{-3} sec. The hydration reaction rate-constants are shown in Table 2.

Determination of Rate Constant k_2. The yellow species 'Y' being unstable in acidic solution it is hydrated at a faster rate and a colourless species S″ is formed.

$$G + H^+ \overset{K}{\rightleftharpoons} Y \xrightarrow{k_2} S'' \quad \text{(colourless)}$$

Kinetic runs were followed by observing the change in absorbance at λ_{max} with time. A_o-values were obtained by extrapolation.

The rate constants k_2 determined by varying concentration of acid are shown in Table 3.
It is noticed that k_2 values are not constant but increase with $[H^+]$.

The values of k_2 were plotted against H^+ and a straight-line was obtained.

Determination of Rate Constant k_3. The decolorization in alkaline solution is due to the reaction:

$$G \xrightarrow[k_3]{+\ OH^-} S''' \qquad \text{(colourless)}$$

TABLE 2. BRILLIANT GREEN CONCENTRATION $= 2.5 \times 10^{-5}$M.

Time (sec)	Optical density at $\lambda_{max} = 628$ nm	$k_I=\frac{2.303}{t}\log_{10}\frac{A_o-A_\infty}{A_t-A_\infty}$ $\times 10^3$/sec
0.00	1.326 A_o	—
60	1.30 A_t	0.32
300	1.19	0.36
1200	0.81	0.40
1800	0.69	0.36
1200	0.59	0.33
3000	0.51	0.31
	0.44 A_∞	

Average $k_I = 0.346 \times 10^{-3}$/sec.

TABLE 3. CONCENTRATION OF BRILLIANT GREEN $= 2.5 \times 10^{-5}$M.

$[H^+] \times 10^2$M	k_2 sec $\times$ 10^3
2.00	4.62
4.00	5.16
6.00	5.43
8.00	5.75
10.00	5.88

TABLE 4. CONCENTRATION OF BRILLIANT GREEN $= 2 \times 10^{-5}$M.

$[OH^-] \times 10^2$M	k_3 sec$^{-1} \times 10^3$
1	1.026
2	1.100
3	1.120
4	1.170
5	1.200

The rate constant values are determined by using varying concentrations of sodium hydroxide as shown in Table 4. The rate of decolorization is proportional to $[OH^-]$.

Visible Absorption Spectra of Brilliant Green in Methanol–Dioxane Mixtures. It has been noticed[4] that carbonium ion dyestuffs are insoluble in nonpolar solvents as well as in solvents of low-polarity. In order to study the spectral changes of Brilliant Green, it was first dissolved in a polar solvent, e.g. methanol, and a solvent having low-polarity was gradually added. The increase in the percentage of the non-polar solvent results in the appearance of an absorption band at shorter wavelength and the extinction coefficient of the longer wavelength absorption band decreases as shown in Fig. 3.

The increase of dioxane intensifies the shorter wavelength absorption band as compared with the longer wavelength absorption. The changes in absorption spectra in the solvent mixtures are similar to that of analogous dyes studied in aqueous media.[5–7] The shorter wavelength absorption has been ascribed to the presence of aggregated dyestuff cations where the longer wavelength absorption band is due to the monomeric species. From the spectral changes it is clear that aggregated dyestuff cation concentration is enhanced in less polar media whereas the presence of the aggregated species in an aqueous solution having the same concentration is shown by a shoulder on the shorter wavelength side of the major absorption peak.

The dyestuff solution in dioxane is not stable and absorbance decreases with time. The rate constant for decolorization is determined. The experimentally determined value is 1.07×10^{-2} sec.

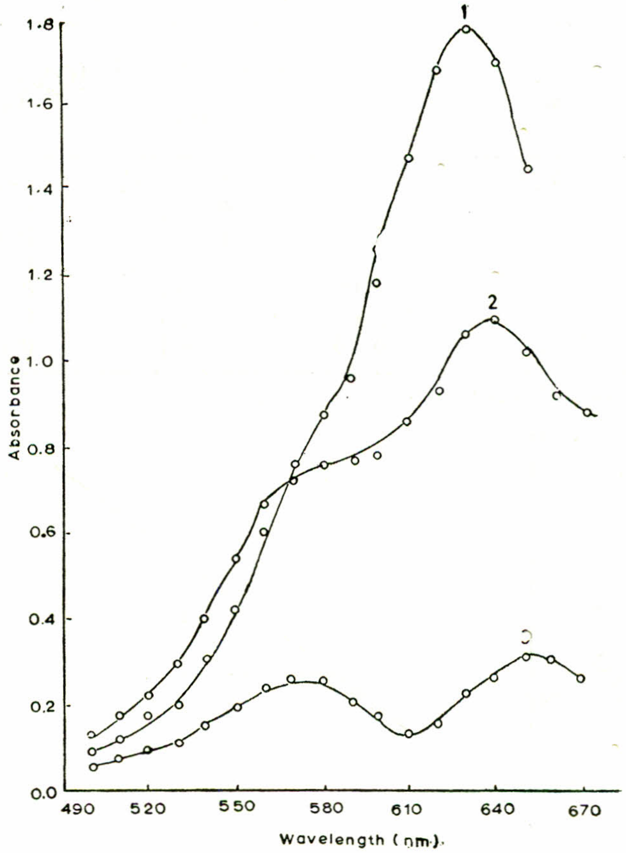


Fig. 3. Absorption spectra of Brilliant Green in dioxane–methanol mixtures (1×10^{-4}M). (1) 5% dioxane, (2) 75% dioxane, (3) 95% dioxane,

Discussion

A comparison between the values of various rate constants of Brilliant Green is interesting. The hydration rate constant k_{I} is 0.346×10^{-3} sec in neutral aqueous solution, whereas the hydration rate in alkaline solution is much faster (about 29–37 times) and hydration process is proportional to the OH^- concentration. The coloured species (sp^2 hybridized) is predominantly displaced towards the colourless (sp^3 hybridized) carbinol. The rate of decolorization in dioxane solution, the rate constant value being 1.07×10^{-2} sec, is similar to that in alkaline medium. In the case of alkaline solution, oxygen of the OH^- is capable of donating a lone-pair of electrons to the carbonium ion with the result a nonresonating tetrahedral compound is formed. On the same basis dioxane behaves as a base where oxygen acts as donor. It interacts with the carbonium cation to form a tetrahedral structure without any charge transfer and thus decolorization is observed.

In presence of acid, one of the—$N(C_2H_5)_2$ groups becomes protonated. The value of equilibrium constant ($K = 140.5\,\mathrm{M}^{-1}$) clearly supports the interaction for the formation of 1:1 adduct. The protonation reaction is instantaneous and the $G + H^+ \rightleftharpoons Y$ equilibrium is strongly displaced towards the monoprotonated yellow species Y. The rate of decolorization of the protonated species is about 13–16 times faster than in neutral solution. The rate constant values increases with the increasing concentration of the acid. All the rate constant values k_{I}, k_2, and k_3 show that the reactions are of the first order.

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