Kinetics of Alkaline Hydrolytic degradation of Brilliant Green Dye in Aqueous Solution

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ABSTRACT

Kinetics of alkaline hydrolytic degradation of Brilliant green (BG) dye in aqueous solution was investigated at 625nm with emphasis on the mechanistic pathway of the reaction with a view to ascertaining the effectiveness of the reaction for the removal of industrial effluents like brilliant green. The hydrolytic reaction was first order dependence with respect to Brilliant green and hydroxyl ion. Michaelis-Menten type kinetics was observed indicating the presence of an intermediate complex during the course of the reaction. The reaction was dependent on the ionic strength of the reaction mixture, revealing $Z_A Z_B$ equals to -1. Activation energy (E_a) was 84.32 kJ mol^{-1} and change in enthalpy of activation ($\Delta H^{\ddagger}$), change in entropy of activation ($\Delta S^{\ddagger}$) and change in free energy of activation ($\Delta G^{\ddagger}$) were 81.77 kJ mol^{-1}, -0.446 kJK^{-1}mol^{-1} and 214.678 kJmol^{-1}respectively. FTIR product analysis revealed the presence of carbinol as the major reaction product and stoichiometric study was achieved via spectroscopic titration. A plausible mechanism was proposed based on the kinetic and spectroscopic results obtained.

Keywords: Brilliant green, Kinetics, Mechanism, Potassium nitrate, Sodium hydroxide.

INTRODUCTION

Brilliant green is amino- based basic dye, which can be classified under triphenyl methane dyes. It serves as an indicator dye because it changes from yellow to green at pH 0-2.6 and it is used to color silk and wool and also serves as antiseptic [1]. It is estimated that about 280,000 tons of textile dyes are released into the environment as industrial effluents world wide [2]. Its presence in industrial effluents poses a serious environmental concern as they are very recalcitrant to microbial degradation [3]. They result to a significant reduction in the photosynthetic activity of aquatic ecosystem [4]. It is, therefore, crucial to treat waste water before discharging them in the form of effluents by chemical oxidation and reduction, physical precipitation, flocculation, photolysis and adsorption. Several adsorption studies have been made which include the use of ozone microbubbles [5], response surface methodology [6], rice husk ash [7], egg shell powder

[8], impregnated bentonite adsorbents   [9], cavitation based hybrid technique   [10],   and iodopolyurethane [11]. However, reports on Brilliant green hydrolysis are very scanty. There are few publications on the hydrolysis in the presence of surfactants [12], among them is the study of Brilliant green hydrolysis in pH 6-11 [13]. Herein is the study on the possibility of breaking down Brilliant green dye via hydrolysis in order to forestall its concomitant hazardous effect.
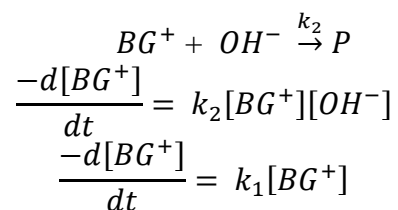
EXPERIMENTAL

Material

Brilliant green dye, sodium hydroxide, potassium nitrate were obtained from Riedel-de-Haen, Germany.

Kinetic procedure

The kinetic study was investigated using a UV-1800 Shimadzu spectrophotometer provided with a thermostated cell, interfaced to a computer. The reaction was carried out via pseudo-first order conditions by maintaining a large excess(x10 or greater) of initial concentrations of sodium hydroxide to that of brilliant green dye. Appropriate quantities in the sequential order of brilliant green, potassium nitrate and sodium hydroxide were measured from stock solutions into the quartz cuvette. A decrease in absorbance of brilliant green dye with time was measured at wavelength 625nm. Pseudo-first order rate constants (k_{obs}) were determined from the slope of a plot of InA versus time

$$BG^+ + OH^- \xrightarrow{k_2} P$$
$$\frac{-d[BG^+]}{dt} = k_2[BG^+][OH^-]$$
$$\frac{-d[BG^+]}{dt} = k_1[BG^+]$$

Where,

$k_1 = pseudo\ first\ order\ rate\ constant(s^{-1})$
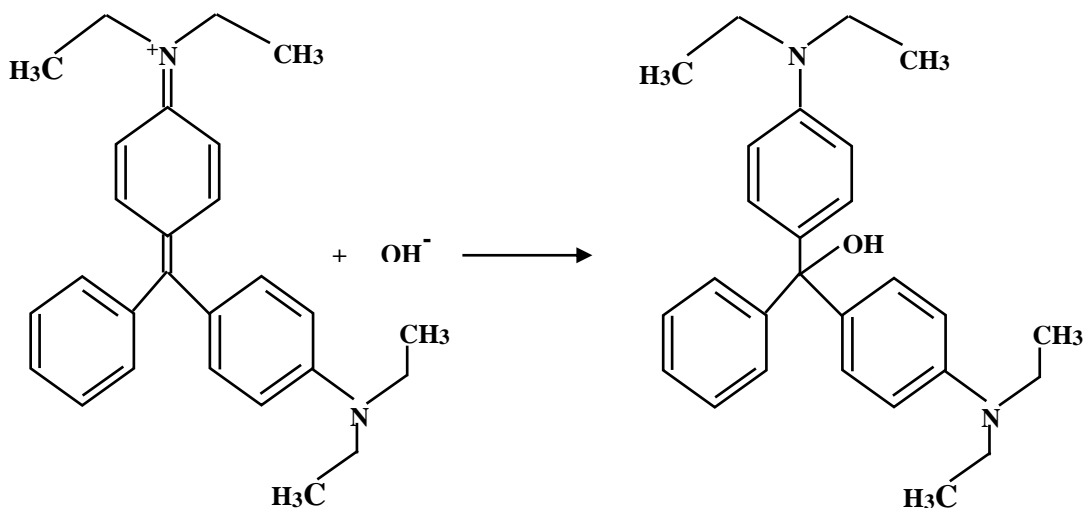$k_2 = second\ order\ rate\ constant(M^{-1}s^{-1})$
$k_1 = k_2[OH^-]$
$k_2 = \frac{k_1}{[OH^-]}$

Stoichiometry and product analysis

The absorbance at infinite time of reaction mixtures containing various initial concentrations of sodium hydroxide (1.00 x 10^{-3} – 4.00 x 10^{-3} mol L^{-1}), fixed initial concentrations of brilliant

green and potassium nitrate at 1×10^{-5} and 0.05 mol L^{-1} respectively were measured. The plot of absorbance versus [NaOH] curve revealed that one mole of brilliant green consumed one mole of sodium hydroxide.

FTIR spectrum suggests the product as carbinol with O-H broad peak 3500-3200 cm^{-1}, which involved OH$^-$ attack on the carbon atom within the planar ring of the dye.

Polymerization

The hydrolytic reaction did not induce polymerization with acrylonitrile monomer solution in an inert atmosphere for 24 h. Further addition of acrylonitrile had no effect on the rate of reaction. This indicates the absence of free radical specie in the course of the reaction [14-19].

RESULTS AND DISCUSSION

The observed rate constant (k_{obs}) increased with [BG] as shown in Table 1. The slope of a plot of In k_{obs} versus In [BG] was one, indicating a first order dependence with respect to [BG].

Table 1: Effect of Brilliant Green Concentration

10^5[BG]/ mol L^{-1}	10^3 k_{obs}/s^{-1}
1.00	0.48
2.00	0.80
3.00	1.13
4.00	1.58
5.00	1.63
6.00	1.91
7.00	2.27

[NaOH] 1.67×10^{-3} mol L^{-1} μ= 0.08 mol L^{-1} T=298K

The kinetic study also showed a first order dependence with respect to [OH⁻] as shown in Table 2. Second order rate constant obtained from the slope of a plot of k_{obs} versus [OH⁻] was 0.479 mol⁻¹L s⁻¹. Plot of $1/k_{obs}$ versus $1/[OH⁻]$ gave an intercept, suggesting the presence of an intermediate complex(Fig. 1).

Table 2: Effect of Hydroxyl ion Concentration

10^3[OH⁻]/ M	$10^3 k_{obs}$/s⁻¹
1.00	0.58
1.33	0.64
1.67	0.84
2.00	0.90
2.50	1.22
3.00	1.48
3.50	1.64
4.00	1.89

[BG] 1 X 10⁻⁵ mol L⁻¹ μ= 0.05M T=298K

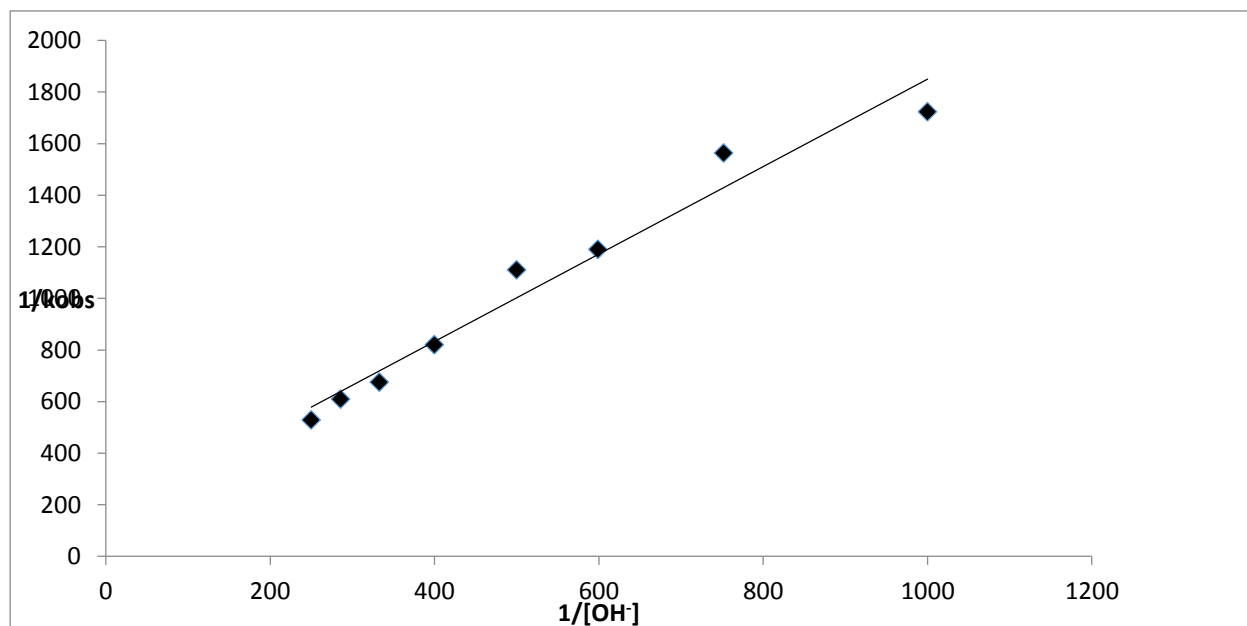Fig. 1: Plot of $1/k_{obs}$ versus $1/$ [OH⁻]

Observed rate constant (k_{obs}) decreased with increase in ionic strength. Consequently, the slope of the plot of log k_{obs} versus $\sqrt{\mu}$ was -1, indicating the presence of -1 and +1 charges on the reactants at the rate determining step (Fig. 2).
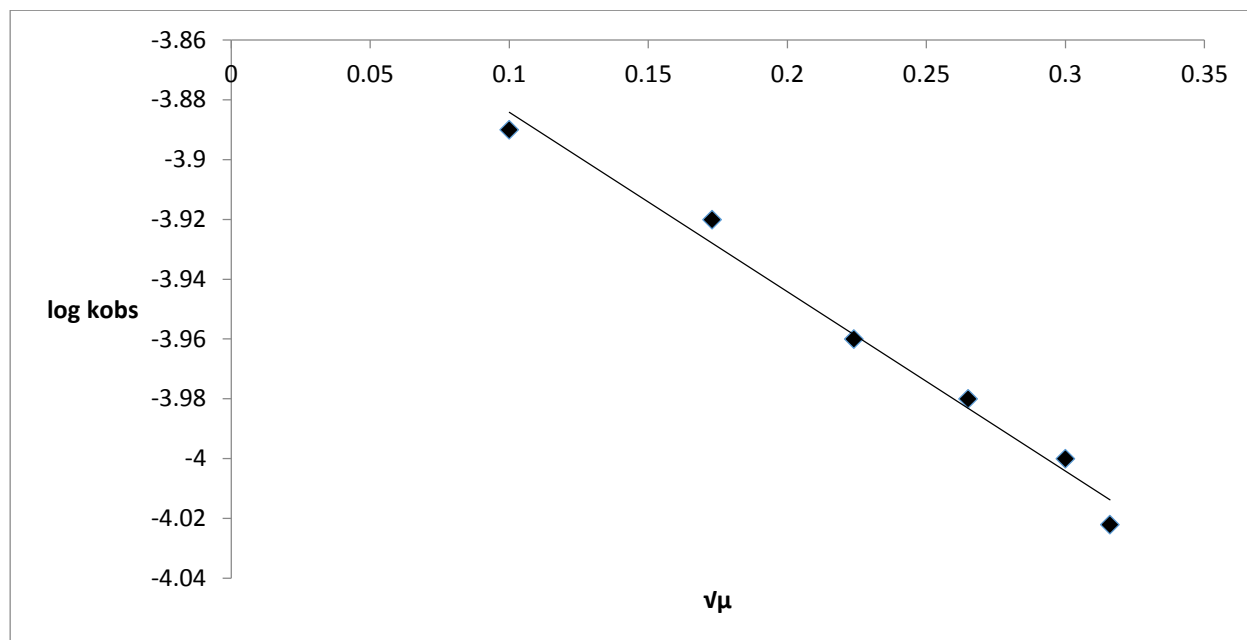
Fig. 2: Plot of log k_{obs} versus $\sqrt{\mu}$ ([BG] 1 X 10^{-5} mol L^{-1} [NaOH] 1.67 X 10^{-3} mol L^{-1} T=298K)

The reaction was studied at different temperature (303-318K) at fixed [BG] 1.00 x 10^{-5}M [NaOH] 1.67 x 10^{-3} mol L^{-1} and μ= 0.095 mol L^{-1}. Increase in k_{obs} with increase in temperature was observed and activation energy (84.32 kJ mol^{-1}) was obtained from the linear Arrhenius plot of In k_{obs} versus I/T. While activation parameters were obtained from the equations below [20]. $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ were 81.77 kJmol^{-1}, -0.446 kJK^{-1}mol^{-1} and 214.678 kJmol^{-1}respectively.

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\left(\frac{k^{/}}{h}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right)$$

$$\ln\left(\frac{k^{/}}{h}\right) = 23.76$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

k = observed rate constant

T= Temperature

$\Delta H^{\#}$= Enthalpy of activation

$\Delta S^{\#}$= Entropy of activation

$\Delta G^{\#}$ = Free Gibb's energy of activation

R= Molar gas constant

$k^{/}$= Boltzmann's constant

h= Plank's constant

On the basis of observed first order dependence with respect to [BG$^+$] and [OH$^-$] and rate of reaction. The experimental rate law is hereby given:

$$\frac{-d[BG^+]}{dt} = k[[BG^+][OH^-]$$

The effect of ionic strength on the rate of reaction can be described according to the theory of Bronsted and Bjerrum. The theory which postulates the reaction through the formation of an activation complex shows the effect of ionic strength on the rate of reaction involving two ions as the relation:

$$Log\ k = \log k_o + 1.02Z_A\ Z_B\sqrt{\mu}$$

The experimental result revealed that Z_AZ_B is equal to -1. This shows that the quantity Z_AZ_B is negative and the rate of reaction decreases with increase in the ionic strength and exhibiting negative slope. Therefore, the Z_AZ_B could be -1 and +1 charges [19, 21]. The negative entropy of activation for the reaction is consistent with a highly organized transition state which depicts an associative mechanism and supports the formation of intermediate complex [22, 23]. Relatively high values of free energy of activation and enthalpy of activation show that the transition state is highly solvated [24]. The mechanism shown below also supports the observed negative entropy of activation. There was no free radical formation as confirmed by the polymerization test as there was no induced polymerization on addition of acrylonitrile to the reaction mixture. Michaelis-Menten plot suggests the presence of an intermediate complex [25].

The mechanism of the reaction involved the rapid attack of the carbon atom within the planar ring of the dye by hydroxyl ions, which consequently resulted into the formation of a complex and finally the product via a slow step.

The mechanism below is proposed based on the kinetic and spectroscopic results:

$$\text{BG}^+ + \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex} \xrightarrow{k_2(\text{slow})} \text{P}$$

$$\text{Rate} = k_2[\text{Complex}] \quad ---------------- (1)$$

$$\frac{d[Complex]}{dt} = k_1[BG^+][OH^-] - k_{-1}[Complex] - k_2[Complex] ----- (2)$$

$$\frac{d[Complex]}{dt} = k_1[BG^+][OH^-] - (k_{-1} + k_2)[Complex] ----(3)$$

$$Applying\ steady\ state\ approximation$$

$$0 = k_1[BG^+][OH^-] - (k_{-1} + k_2)[Complex] ---------- (4)$$

$$k_1[BG^+][OH^-] = (k_{-1} + k_2)[Complex] ------------ (5)$$

$$[Complex] = \frac{k_1[BG^+][OH^-]}{k_{-1} + k_2} --------------(6)$$

$$Substituting\ equation\ (6)\ in\ (1)$$

$$Rate = \frac{k_1 k_2[BG^+][OH^-]}{k_{-1} + k_2}$$

$$Where\ k = \frac{k_1 k_2}{k_{-1} + k_2}$$

$$Rate = k[BG^+][OH^-]$$

CONCLUSION

Alkaline hydrolysis of Brilliant green dye is first order with respect to the concentration of Brilliant green and also first order to the hydroxyl ion concentration. The hydrolytic reaction involves attack on the carbon within the planar ring of the dye by hydroxyl ion, which results to the destruction of the conjugation configuration of the dye. Brilliant green dye is best removed from industrial effluents by hydrolytic reaction being the fastest, least cost effective techniques compared to photolytic and adsorption methods.

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