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KINETICS AND MECHANISM OF REDOX REACTION OF BRILLIANT GREEN WITH BROMATE ION IN AQUEOUS ACIDIC MEDIUM

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ABSTRACT

The kinetics and mechanism of the redox reaction of brilliant green dye, [BG^+], with bromate ion, [BrO_3^-], has been investigated spectrophotometrically in aqueous tetraoxosulphate(VI) acid medium under pseudo – first order condition at 28±1 ºC, [H^+] = 1.0×10^{-2}moldm^{-3}, I = 0.30 coulomb^{2}moldm^{-3}(Na_2SO_4) and λ_{max} = 622 nm. The reaction was first order with respect to [BG^+] and [BrO_3^-] and a stoichiometric mole ratio determination of [BG^+] with [BrO_3^-] is 1:1. The rate of reaction was acid dependent but was not significantly affected by changes in ionic strength and dielectric constant of the medium. Added ions catalyzed the rate of reaction and Michaelis-Menten's plot started from the origin. Thus, an outer-sphere mechanism was proposed based on the results obtained from spectroscopic studies, effect of added ions and kinetic evidences from Michaelis-Menten's plot.

Keywords: Brilliant green, Bromate ion, Kinetics, Mechanism, Redox.

INTRODUCTION

Brilliant green or Zelenka (also known as Emerald Green) with a molecular formula of$C_{27}H_{33}N_2HO_4S$is a triarylmethane dye [1]. It is an odourless yellow-green to green powder which is toxic and has mutagenic and carcinogenic effects that affect aquatic biota and humans; with a melting point of 210 °C (410 °F; 483 K) and an absorbance maximum, λ_{max} at 622 nm [2]. Brilliant green is a visible light-activated photocatalyst in organic synthesis [3]. It is used extensively in textile dying and for the production of cover paper in the paper industry [4,5]. Brilliant green induces vomiting when swallowed and toxic when ingested [6].

Bromate is an inorganic ion which naturally exists in water reservoirs due to reaction of bromide ion with ozone [7]. Potassium salts of bromate have wide applications in different textile and food industries [8, 9]. Investigation declares reduction of bromate in water to yield bromide by the reaction with reduced forms of iron i.e Fe(II), and, or, Fe(0) [10, 11].

Bromate with redox potential of 1.44 V [12] is a valuable chemical reagent, widely used as a powerful oxidizing agent. Kinetics of its reactions in acidic media is complex. In acidic medium, bromate has been widely used in the oxidation of various organic and inorganic compounds [13-20]. Oxidation of aquoiron(II) by bromate has been reported [21]. Oxidation of various metal ions by bromide ion has also been reported [22-26]. Several photocatalytic degradation procedures for the decolourization of triarylmethane dyes have been reported in the literatures [27-29], but the redox reaction of brilliant green dye with bromate ion has not received an attention.

Therefore, in this report, we investigate the kinetics and mechanism of redox reaction of brilliant green dye with bromate ion, which hitherto has not been reported, resulting in the paucity of literatures concerning its kinetic data and result of this study could be of importance in improving on its uses and safer handling or treatment of the industrial effluents from the brilliant green dye.

MATERIALS AND METHODS

All the reagents were Analar grade and used without further purification. Brilliant green dye (Merck) and the oxidant, sodium bromate (BDH) were used. The source of hydrogen ions was tetraoxosulphate(VI) acid(BDH) and sodium sulphate (BDH) was used to maintain the ionic strength of the reaction medium. All other reagents such as sodium nitrate (NO_3^-), sodium methanoate ($HCOO^-$), magnesium sulphate (Mg^{2+}), calcium sulphate (Ca^{2+}) which were used to test for the effect of added ions, were all used as supplied. Acetone- water mixture was used to test for the effect of dielectric constant and acrylamide with methanol were used to test for free radicals in the reaction. Kinetic runs were made using Sherwood Colorimeter 254 and the reaction was monitored with a digital stop watch.

Aqueous solutions of Brilliant green dye of desired concentration were freshly prepared prior to use. Standard stock solution of tetraoxosulpate(VI) acid (BDH) of 0.2 mol $dm^{-3}$was prepared by diluting 0.6 cm^3tetraoxosulphate(VI)acid (specific gravity 1.83 gcm^{-3}) in a 100 cm^3

volumetric flask and making up to the mark with distilled water. The solution was standardized volumetrically using Na_2SO_3 as a primary standard and methyl orange as indicator. Stock solution of 1.0 mol dm^{-3}sodium bromate was prepared by accurately weighing 12.79 g of the salt and dissolving it in distilled water in a 100 cm^{-3} volumetric flask and made up to the mark. Standard solutions of $MgSO_4$, $NaNO_3$, Na_2SO_4, $CaSO_4$ and HCOONa were all prepared by weighing known amount and dissolving in known volume of distilled water.

THE REACTION STOICHIOMETRY

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method [30]. This was done by measuring the absorbance of solution containing various concentrations of bromate ion (0.2–2.0) $\times 10^{-4}$ $moldm^{-3}$, $[H^+]=1.0\times10^{-2}moldm^{-3}$, $I=0.30coulomb^2moldm^{-3}$($Na_2SO_4$) and at constant concentration of Brilliant green $=1.0 \times 10^{-4}moldm^{-3}$. After the reaction had gone to completion, plot of absorbance against mole ratio was done and the point of inflection in the plot gave the number of moles of the Bromate ion consumed by 1 mole of the Brilliant green dye.

THE KINETIC MEASUREMENTS

The kinetic studies were carried out under pseudo–first order conditions with the Bromate ion in excess over the Brilliant green dye at 622 nm, $[H^+] = 1.0 \times 10^{-2}moldm^{-3}$and at 28±1 ^{o}C. The first order rate constants, k_{obs}, were obtained from the plots of log (A_t - $A\infty$) against time t. Where A_t and A_∞ are the absorbances at time t and the end of the reaction respectively.

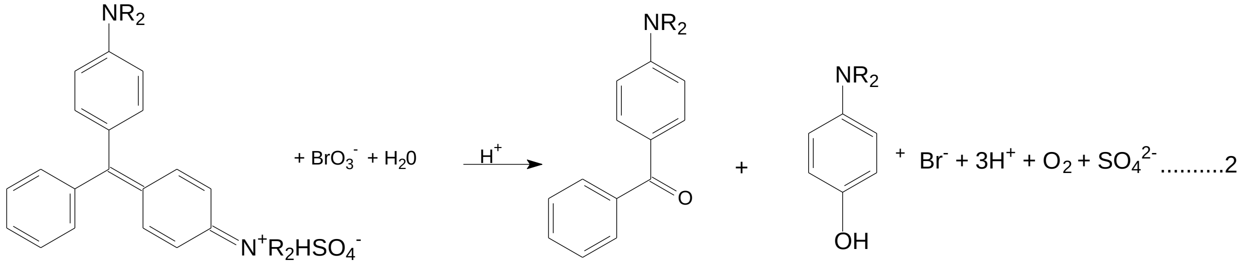
The second order rate constants, $k_2$were obtained using the equation:

$$k_2 = \frac{k_{obs}}{[BrO_3^-]} \qquad (1)$$

RESULTS AND DISCUSSION

STOICHIOMETRIC STUDIES

The stoichiometric studies result indicates one mole of brilliant green reacts with 1 mole of bromate ion as shown in Equation (2):



Similar stoichiometry has been reported in the reaction of bromate ion [31-34].

ORDER OF THE REACTION

A plot of log k_{obs} against log $[BrO_3^-]$ was plotted, the gradient was calculated and k_{obs} was determined. The plot was linear with a slope of0.98 showing that the reaction is first order with respect to $[BrO_3^-]$ and a second order over all. The rate equation for the reaction is

$$\frac{-d[BG^+]}{dt}=k_2[BG^+][BrO_3^-] \qquad (3)$$

EFFECT OF $[H^+]$

The effect of changes in $[H^+]$ on the reaction rate was studied in the range of $(0.1 - 1.5)\times10^{-1}$ $moldm^{-3}$, keeping ionic strength and other reactant concentrations constant. The rate of reaction increased with increase in $[H^+]$. The order of reaction with respect to $[H^+]$ was obtained as the slope of the plot of log k_{obs} against log $[H^+]$. A plot of k_2 against $[H^+]$ gave a linear plot with no intercept. The result indicates acid dependence of rate which is in agreement with the equation,

$$k_{H^+}=a[H^+] \qquad (4)$$

The overall rate equation can be represented by

$$\frac{-d[BG^+]}{dt}= a[H^+][BG^+][BrO_3^-] \qquad (5)$$

Similar result was reported by Singh and Bano [2], on the mechanistic aspects for the oxidation of Brilliant green dye by Chloramine-T in the presence of perchloric acid: a spectroscopic kinetic approach.

Effect of Ionic Strength

The effect of ionic strength on the reaction rate was studied over the (0.1-0.7) mol dm^{-3} range using Na_2SO_4, keeping the concentrations of all other species in the reactions mixture constant. Ionic strength has negligible effect on the rate of reaction [35, 36].

Effect of Dielectric Constant

The effect of dielectric constant (D) on the reaction rate was investigated in the range of 80.10 – 56.72 using $(CH_3)_2CO$-H_2O mixtures. The reaction rate constants obtained were practically unchanged indicating lack of dependence of rate on dielectric constant.

Effect of Added ions

Added cations (Mg^{2+} and Ca^{2+}) and anions (NO_3^- and $HCOO^-$) increased the rate of reaction. It could imply that the rate determining step involves species with formal charges and this is an indication that the reaction might be operating via the outer sphere mechanism because lack of catalysis by the added ions has been attributed to reactions operating via inner-sphere mechanism. Similar ion catalysis has been reported for reactions operating via outer sphere mechanism [37, 38].

Test for intermediate complex formation

Reaction mixtures were made and spectra of the product recorded immediately over a range of wavelength (400-650nm). From the recorded spectra, there was no shift in λ_{max} as compared with that of the brilliant green dye solution.

The Michaelis-Menten's plot of $1/k_{obs}$ against $1/[BrO_3^-]$ gave a straight line starting from the origin. This suggests that there was no intermediate complex formation with appreciable equilibrium constant during the course of the electron transfer.

Polymerization Studies

Acrylamide was added to the partially reacted solution and to the reactants separately to initiate free radical polymerization in the presence of large excess of methanol. There was formation of gelatinous precipitate and this indicates the presence of free radical in the reaction mixtures.

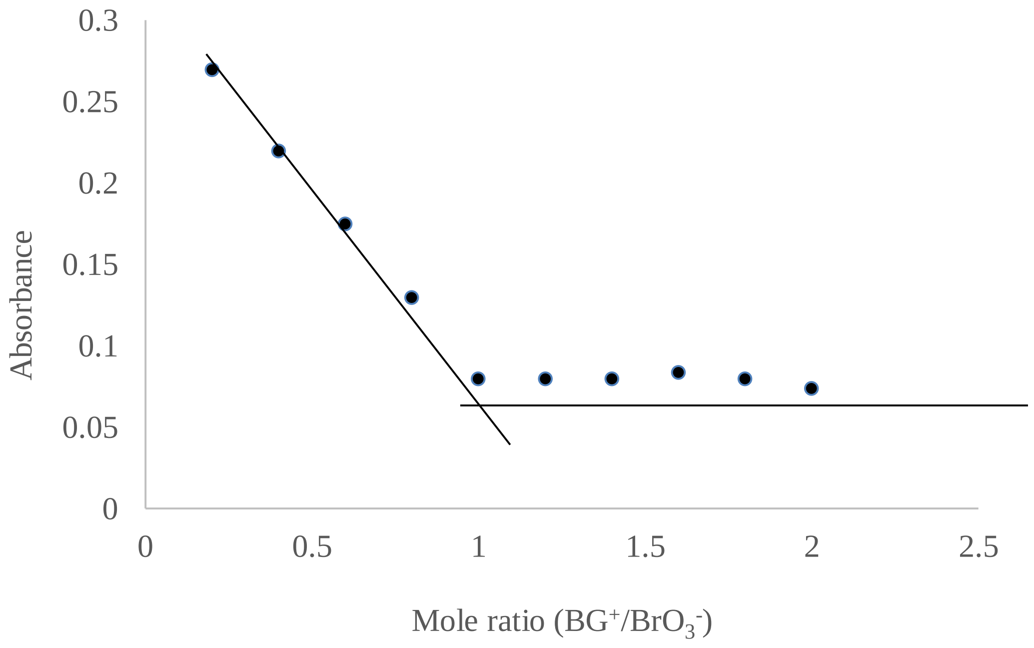


Figure 1: Plot of the Stoichiometry for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.30$ coulomb^2 mol dm^{-3}(Na_2SO_4), $[BrO_3^-] = (0.2 – 2.0) \times 10^{-4}$ mol dm^{-3}, $[H^+] = 0.01$ mol dm^{-3}, $\lambda_{max} = 622$ nm, and T = 28 ± 1°C.

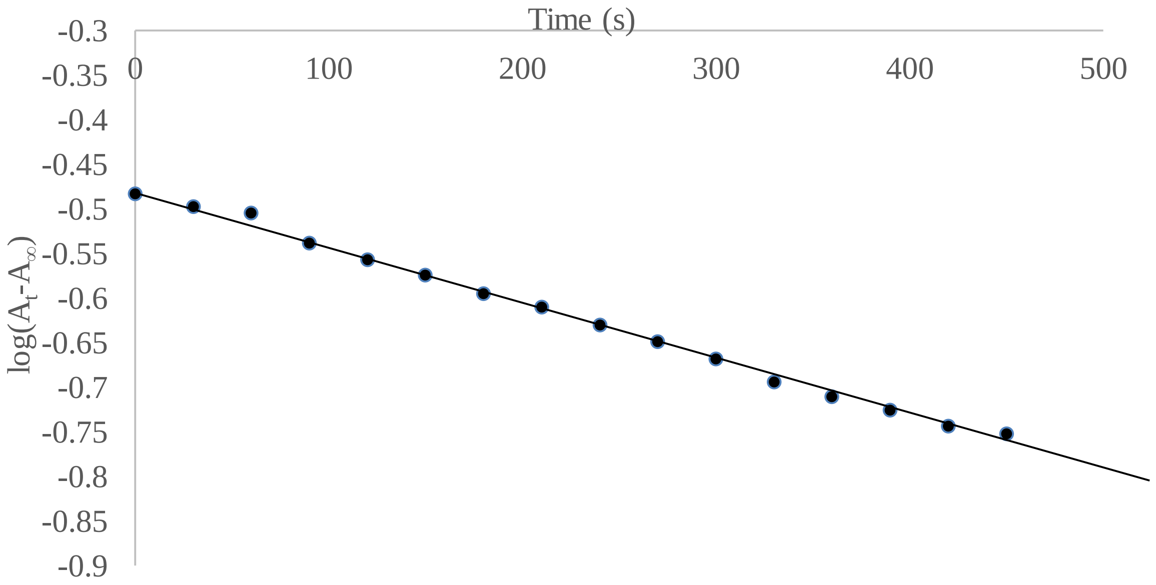


Figure 2: Typical Pseudo-first Order Plot for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$mol dm^{-3}, $\mu = 0.3$ coulomb^2 mol dm^{-3} (Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1 ℃, and $\lambda_{max} = 622$ nm.

Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.3$ coulomb^2 mol dm^{-3}(Na_2SO_4), T = 28 ± 1°C and λ_{max}= 622 nm

$10^2[BrO_3^-]$, mol dm^{-3}	$10^1[H^+]$, mol dm^{-3}	$10^4 k_{obs}$, s^{-1}	$10^1 k_2$, dm^3 mol^{-1} s^{-1}
1.0	0.1	21.30	2.13
1.1	0.1	23.87	2.17
1.2	0.1	26.76	2.23
1.3	0.1	28.73	2.21
1.4	0.1	31.50	2.25
1.5	0.1	34.20	2.28
1.6	0.1	36.16	2.26
1.7	0.1	37.91	2.23
1.8	0.1	41.04	2.28
1.5	0. 3	34.20	2.28
1.5	0.3	34.65	2.31
1.5	0.5	35.40	2.36
1.5	0.7	35.70	2.38
1.5	0.9	36.15	2.41
1.5	1.1	36.60	2.44
1.5	1.3	37.05	2.47
1.5	1.5	37.50	2.50

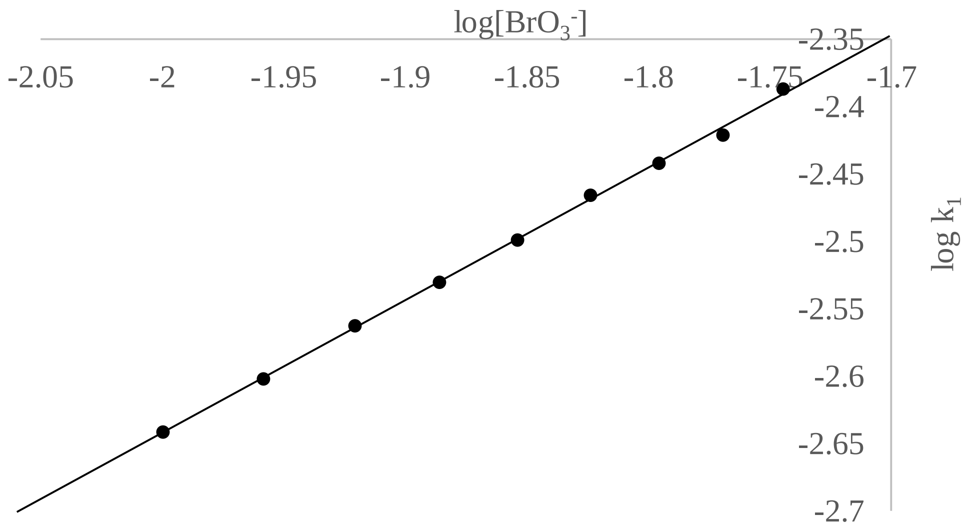


Figure 3: Plot of logk_{obs} versus log$[BrO_3^-]$ for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = (1.0 – 1.8) \times 10^{-2}$ mol dm^{-3}, $\mu = 0.3$ coulomb^{2}mol dm^3(Na_2SO_4), $[H^+] = 0.01$mol dm^{-3} , T = 28 ± 1°C, and λ_{max} = 622 nm

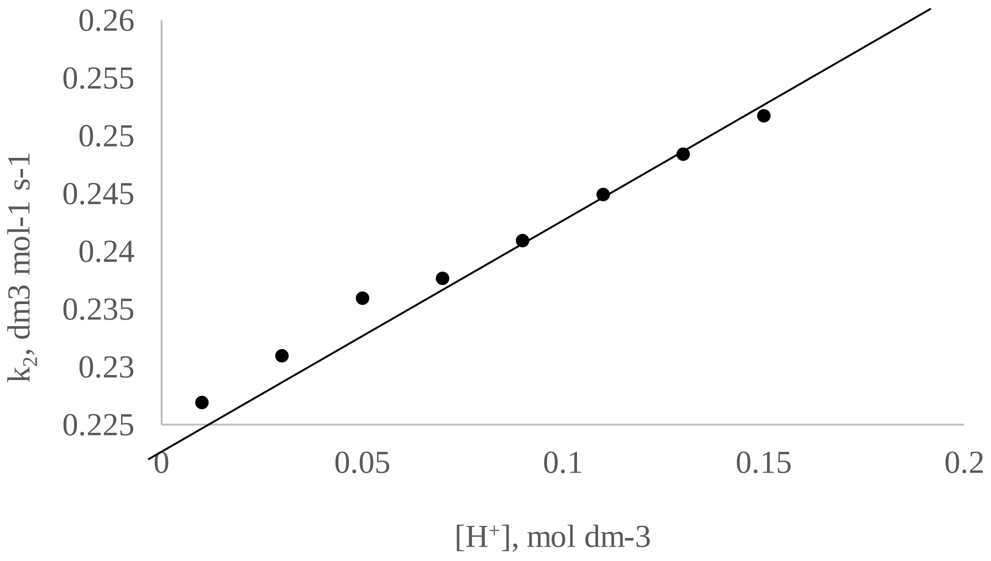


Figure 4: Plot of $k_2(H^+)$ versus $[H^+]$ for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.3$ coulomb^2 mol dm^{-3}(Na_2SO_4), T = 28 ± 1°C, and $\lambda_{max} = 622$ nm

Table 2: Effect of Change in Ionic Strength on Rate Constants for the Reaction of BG^+andBrO_3^-at $[BG^+]$ =1.0 ×10^{-4} mol dm^{-3}, $[BrO_3^-]$ = 1.5×10^{-2} mol dm^{-3},μ = (0.1 – 0.7) coulomb^2 mol dm^{-3}(Na_2SO_4), $[H^+]$ = 0.01 mol dm^{-3}, T = 28 ± 1°C and λ_{max}= 622 nm,

μ, coulomb^2 mol dm^{-3}	$10^4 k_{obs}$, s^{-1}	$10^1 k_2$dm^3 mol^{-1} s^{-1}
0.1	34.05	2.27
0.2	33.90	2.26
0.3	34.20	2.28
0.4	34.20	2.28
0.5	33.90	2.26
0.6	33.75	2.25
0.7	34.35	2.27

Table 3: Effect of Change in the Dielectric Constant of Reaction Medium on the Rate Constants for the Reduction of BG^+ with BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, μ = 0.3 coulomb^2 mol dm^{-3} (Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1 ℃, and $\lambda_{max} = 622$ nm

D	10^4k_{obs}, s^{-1}	10^1k_2, dm^3 mol^{-1} s^{-1}
80.10	34.05	2.27
79.02	34.35	2.29
76.47	34.20	2.28
71.40	34.20	2.28
61.25	34.05	2.27
56.72	33.90	2.26

Table 4: Effect of Added Anions to the Reaction Medium on the Rate Constants for the Reduction of BG^+withBrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, μ = 0.3 coulomb^{2}mol dm^{-3}(Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1℃, and $\lambda_{max} = 622$ nm

Ion	10^3[Ion],mol dm^{-3}	10^4k_{obs}, s^{-1}	10^1k_2, dm^3 mol^{-1} s^{-1}
NO_3^-	0.00	34.20	2.28
	10.00	41.55	2.77
	20.00	48.45	3.23
	30.00	63.90	4.26
	40.00	71.70	4.78
	50.00	76.20	5.08
	60.00	86.85	5.79
	70.00	90.45	6.03
$HCOO^-$	0.00	34.05	2.27
	10.00	40.35	2.69

20.00	52.35	3.49
30.00	58.65	3.91
40.00	63.90	4.26
50.00	71.40	4.76
60.00	75.90	5.06
70.00	81.60	5.44

Table 5: Effect of Added Cations to the Reaction Medium on the Rate Constants for the Reduction of BG^+ with BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.3$ $coulomb^2$ mol dm^{-3}(Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1 °C, and $\lambda_{max} = 622$ nm

Ion	10^3[Ion],mol dm^{-3}	10^4k_{obs}, s^{-1}	10^1k_2, dm^3 mol^{-1} s^{-1}
Mg^{2+}	0.00	34.20	2.28
	10.00	37.80	2.52
	20.00	41.10	2.74
	30.00	48.75	3.25
	40.00	51.15	3.41
	50.00	55.95	3.73
	60.00	61.65	4.11
	70.00	64.20	4.28
Ca^{2+}	0.00	34.20	2.28
	10.00	38.55	2.57
	20.00	46.65	3.11
	30.00	57.15	3.81
	40.00	61.80	4.12
	50.00	66.30	4.42
	60.00	70.95	4.73
	70.00	73.80	4.92

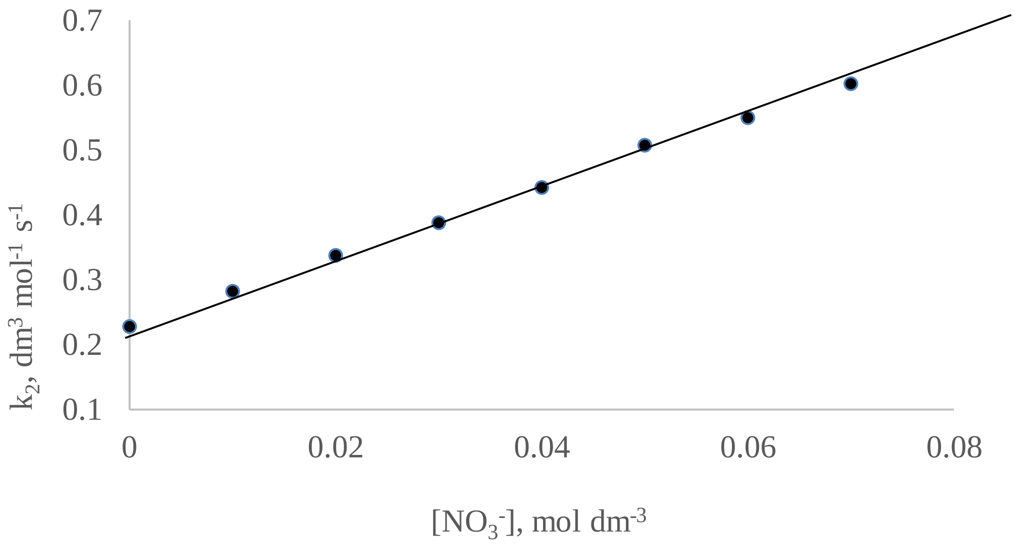


Figure 5: Plot of $k_2(NO_3^-)$ versus $[NO_3^-]$ for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, $[NO_3^-] = (10.0 – 70.0) \times 10^{-3}$ mol dm^{-3}, $\mu = 0.3$ coulomb^{2}mol dm^{-3}(Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1°Cand $\lambda_{max} = 622$ nm

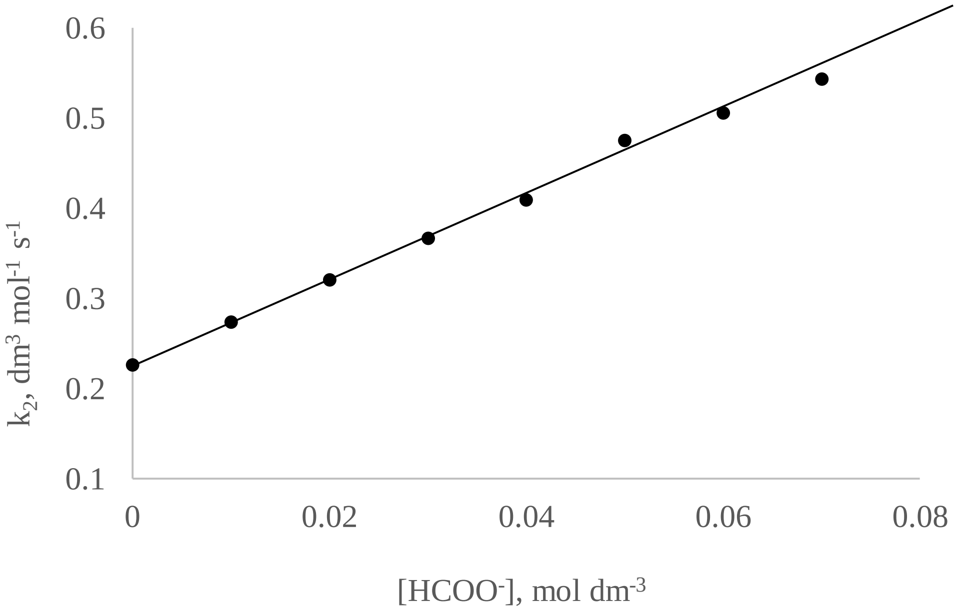


Figure 6: Plot of $k_2(HCOO^-)$ versus $[HCOO^-]$ for the Reaction of BG^+ and BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, $[HCOO^-] = (10.0 – 70.0) \times 10^{-2}$ mol dm^{-3}, $\mu = 0.3$ coulomb^{2}mol dm^{-3} (Na_2SO_4),$[H^+] = 0.01$ mol dm^{-3}, T = 28 ± 1°C and $\lambda_{max} = 622$ nm

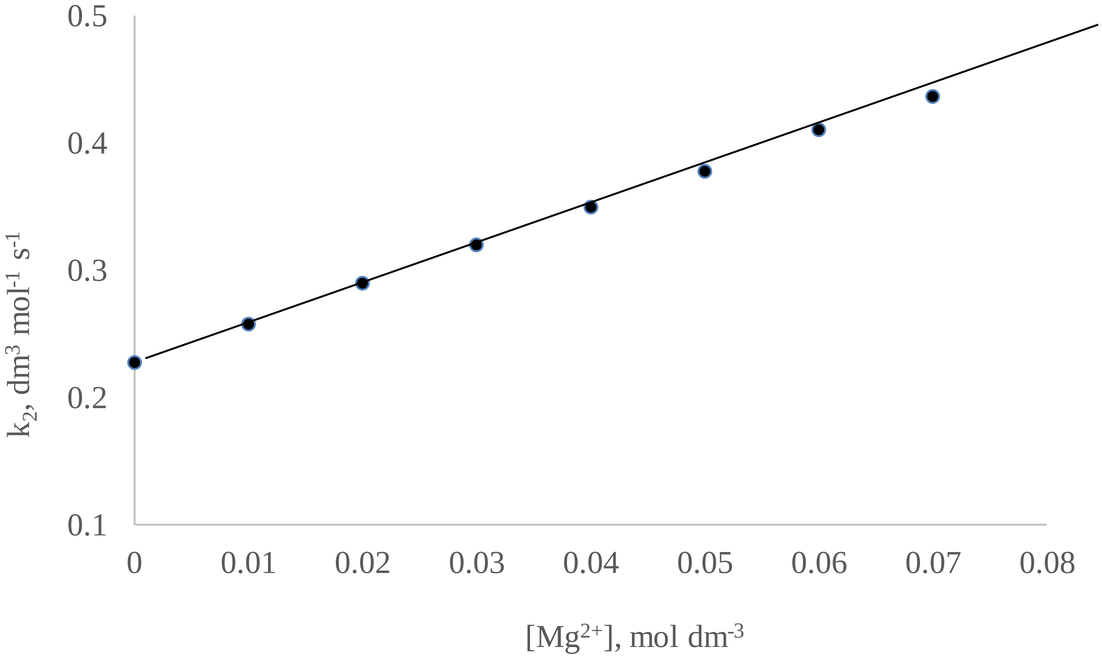


Figure 7: Plot of $k_2(Mg^{2+})$ versus $[Mg^{2+}]$ for the Reaction of BG^+ and BrO_3^-at $[BG^+] = 1.0\times10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5\times10^{-2}$ mol dm^{-3},$[Mg^{2+}] = (10.0 – 70.0) \times10^{-3}$ mol dm^{-3}, μ = 0.3 coulomb^{2}mol dm^{-3}(Na_2SO_4), $[H^+]$ = 0.01 mol dm^{-3}and λ_{max} = 622 nm

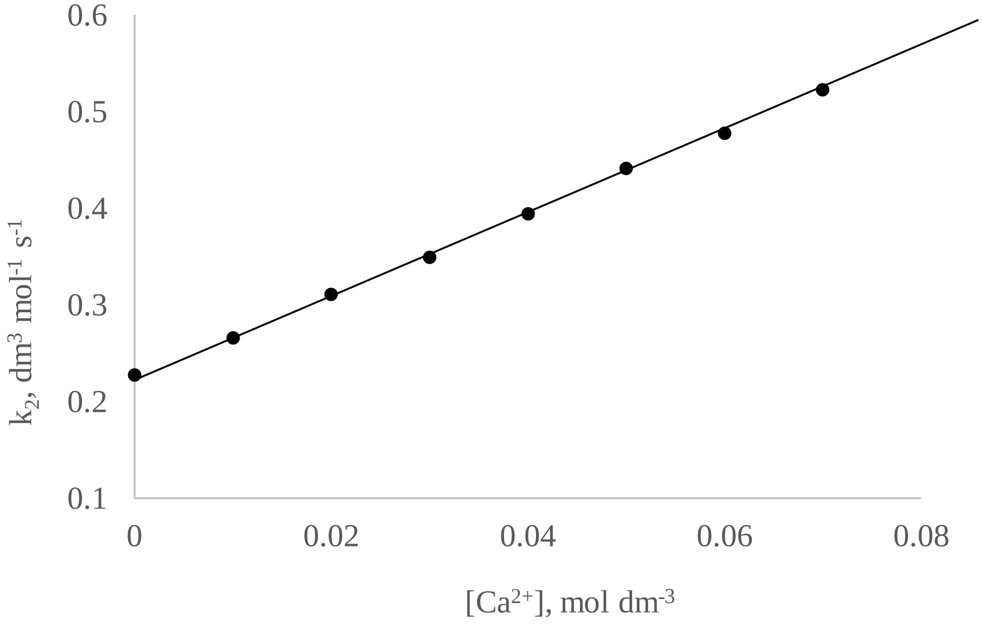


Figure 7: Plot of $k_2(Ca^{2+})$ versus $[Ca^{2+}]$ for the Reaction of BG^+ and BrO_3^-at $[BG^+] = 1.0\times10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times10^{-2}$ mol dm^{-3}, $[Ca^{2+}] = (10.0 – 70.0) \times10^{-3}$ mol dm^{-3}, μ = 0.3 coulomb^{2}mol dm^{-3}(Na_2SO_4), $[H^+]$ = 0.01 mol dm^{-3}and λ_{max} = 622 nm

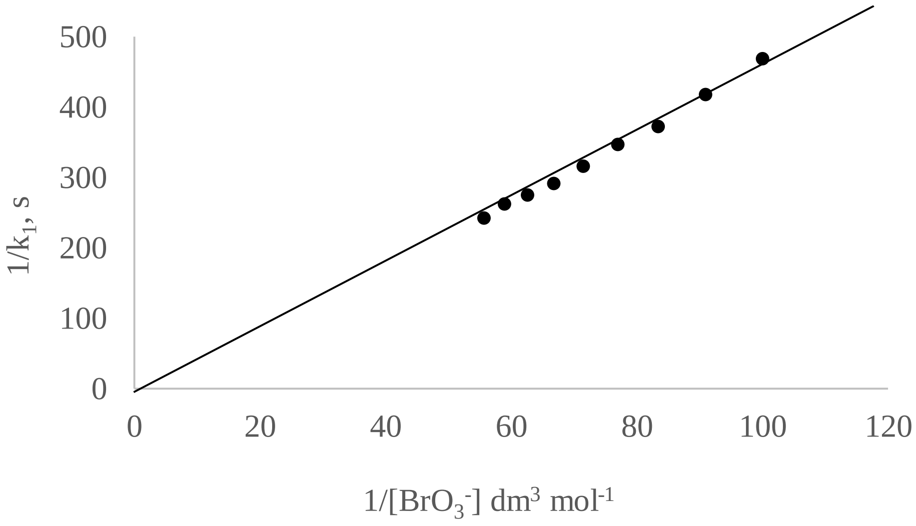
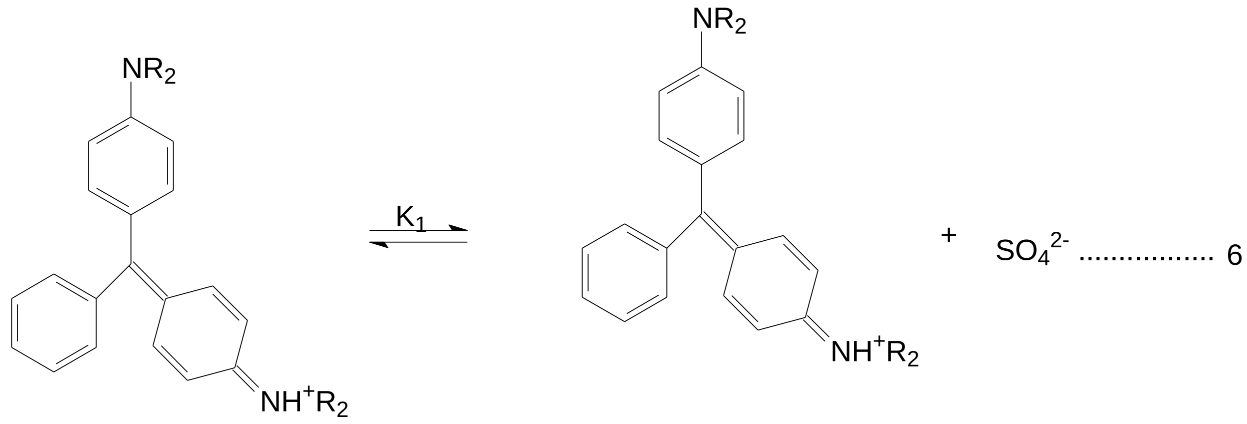
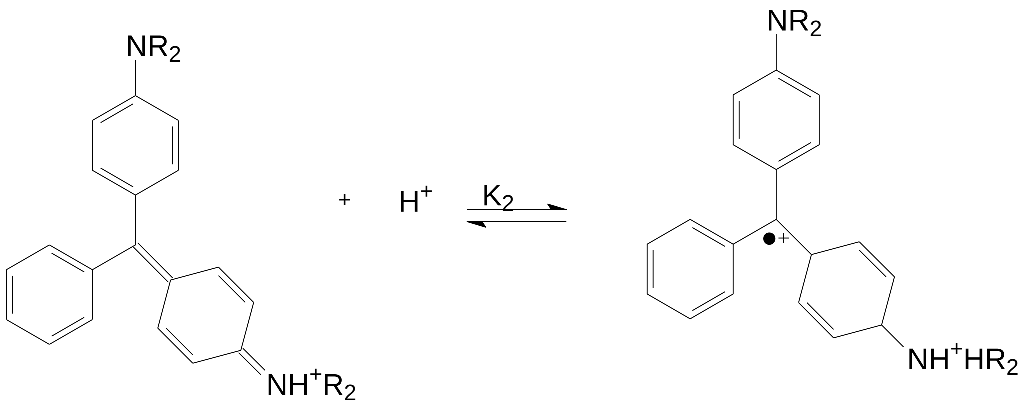


Figure 8: Michaelis-Menten's Plot of $1/k_{obs}$ versus $1/[BrO_3^-]$ for the Reduction of BG^+ by BrO_3^- at $[BG^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[BrO_3^-] = 1.5 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.3$ coulomb^{2}mol dm^{-3}(Na_2SO_4), $[H^+] = 0.01$ mol dm^{-3},T = 28 ± 1℃ and $\lambda_{max} = 622$ nm

Reaction Mechanism

Based on the results obtained, the mechanism of the reaction can be proposedas:





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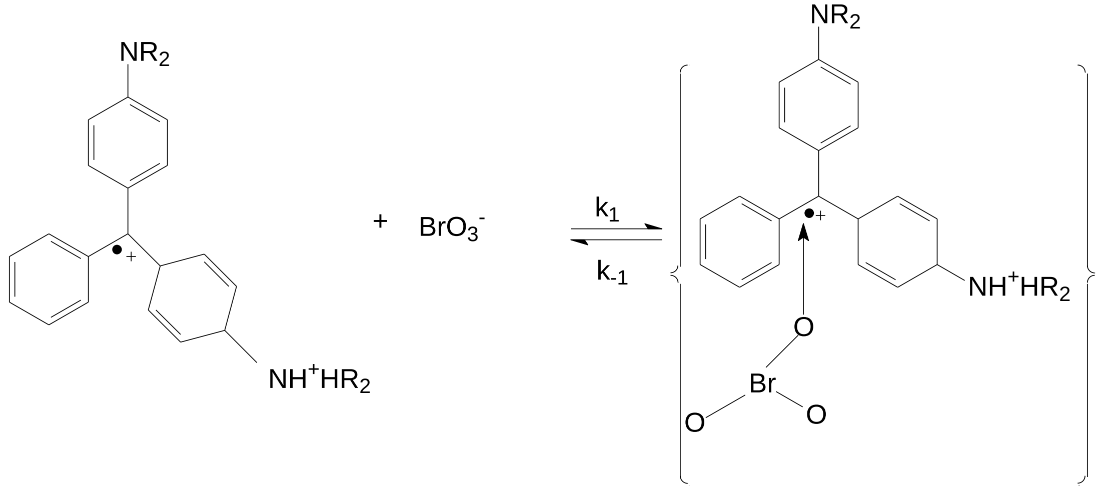

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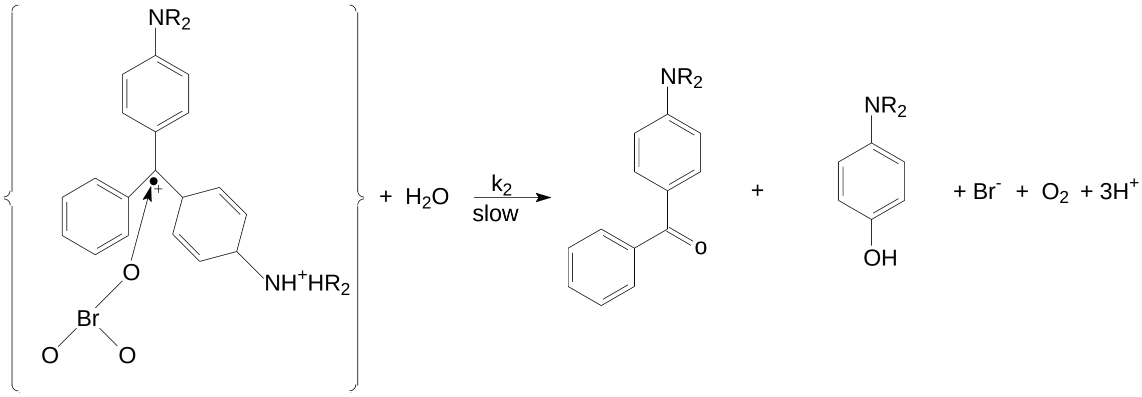

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Rate=k$_2$[I.M][H$_2$O] 10

where [H$_2$O] = 1

Rate = k$_2$ [I.M] 11

Apply steady state approximation

$k_1 [I.B][BrO_3^-]- k_{-1} [I.M]= 0$ 12

$k_1 [I.B][BrO_3^-] = k_{-1} [I.M]$ 13

$[I.M] = \frac{k_1[I.B][BrO_3^-]}{k_{-1}}$ 14

From equation 2,

$[I.B] = K_2 [BG^+][H^+]$ 15

Substitute equation 10 into 9

$[I.M] = \frac{k_1K_2[BG^+][BrO_3^-][H^+]}{k_{-1}}$ 16

Substitute equation 16 into 6

$\text{Rate} = \frac{k_2k_1K_2[BG^+][BrO_3^-][H^+]}{k_{-1}}$ 17

$\text{Rate} = k_{obs}[BG^+][BrO_3^-]$ 18

where $k_{obs} =\frac{k_2k_1K_2[H^+]}{k_{-1}}$

N/B

R = Ethyl group ($-CH_2CH_3$)

BG^+ = The dissociated specie formed at Equation (6)

I.B = The activated specie formed at Equation (7)

I.M = The intermediate formed at Equation (8)

The reaction rate was unpertubed at the concentration that was used in carrying out the research, i.e, the dye was stable within that concentration. But, when the concentration was raised, it led to an increase in the reaction rate as shown in the Figure 4.

CONCLUSION

The redox reaction of brilliant green dye with bromate ion in aqueous acidic medium showed a stoichiometry of 1:1. The reaction is second order overall. The reaction showed acid dependent pathway. It also displayed a lack of primary salt effect because ionic strength did not affect rate of reaction. Both kinetic and spectroscopic investigations showed evidence of intermediate complex formation. Based on the foregoing, the outer sphere mechanism is proposed as the plausible mechanistic pathway for this reaction.

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