

Electron Transfer Reaction and Mechanism of Crystal Violet with Bromate Ion in Aqueous Hydrochloric Acidic Medium

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Abstract: Electron transfer reaction between crystal violet and bromate ion have been investigated in aqueous hydrochloric acid medium at $28 \pm 1^\circ\text{C}$. The overall rate of the reaction can be represented as $\frac{d[\text{CV}^+]}{dt} = a [\text{H}^+][\text{BrO}_3^-]$ [CV⁺]. The rate of the reaction was found to be dependent on changes in ionic strength of the reaction medium in the range of $0.1 \leq I \leq 0.7 \text{ mol dm}^{-3}$. Added Mg^{2+} catalyzed the reaction whereas added SO_4^{2-} inhibited the rate of the reaction. On the basis of the result obtained the outersphere mechanistic pathway is proposed for this reaction.

Key words: Bromate • Crystal violet • Kinetics • Ionic strength • Reaction rate

INTRODUCTION

Crystal violet belongs to a group of dyes called Triphenylmethane dyes and is soluble in both cold and hot water, with a melting point of 205°C (478K) and a λ_{max} value of about 589-594 nm [1]. It is widely used as a dye as a biological stain in human and veterinary medicine [2]. It also finds use in several industrial processes for different applications mostly as a textile dye [3]. It is believed that CV is harmful both to human health and animals [4]. Crystal violet's electron transfer reaction with various oxidants has not been extensively studied as very few relevant kinetic data exists in literature. To this end we investigated its electron transfer behavior with bromate ion in aqueous acidic medium and provide a probable mechanistic pathway.

MATERIALS AND METHODS

0.001M Crystal violet stock solution was prepared by dissolving 0.0040799 g in 10 ml of distilled water in a volumetric flask, while 1.6701 g of potassium bromate was weighed using an analytical balance which was dissolved with distilled water and was made up to volume in a 100 ml volumetric flask. The $\lambda_{\text{max}} = 530 \text{ nm}$ of CV was determined by running the electronic spectrum of solution of in the

wavelength range of 400-700 nm [5]. 0.5 M NaCl was used to maintain the ionic strength of the medium and 1.0 mol dm^{-3} HCl solution was used to investigate the effect of hydrogen ion on the rate of the reaction.

Stoichiometry: The stoichiometry of the reaction was investigated using the mole ratio method [6]. The concentration of crystal violet was kept constant at $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 530 \text{ nm}$ while that of bromate ion was varied in the range $(4 - 28) \times 10^{-3} \text{ mol dm}^{-3}$. The absorbance of the reacting mixtures was measured after the reaction had gone to completion. A point of inflexion on the curve of the absorbance versus mole ratio corresponds to the stoichiometry of the reaction.

Kinetic Measurements: The rate of reaction was properly monitored using Photoelectric Colorimeter SM 202. The rate of the reaction of [CV⁺] with [BrO₃⁻] was studied by monitoring the decrease in absorbance of the reaction mixture at wavelength $\lambda_{\text{max}} = 530 \text{ nm}$ characteristic of the reductant [7]. All kinetic runs were carried out under pseudo-first order conditions with respect to oxidant at least 100 folds in excess over the reductant concentration at $28 \pm 1^\circ\text{C}$ and $I = 0.50 \text{ mol dm}^{-3}$ of the reaction medium. The pseudo-first order plots of $\log (A_t - A_\infty)$ versus time were

made and from the slope of the plots, the pseudo-first order rate constant (k_1) was determined. The second order rate constant (k_2) was obtained from the relation $k_1 / [\text{BrO}_3^-]$.

Effect of Change in Hydrogen Ion Concentration, Ionic Strength and Added Ions: The effect of changes in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentration of the other reactants constant while varying the hydrogen ion concentrations in the range $(0.6 - 2.6) \times 10^{-2} \text{ mol dm}^{-3}$. The effect of ionic strength on the rates of the reaction was studied over a range of $(1.0 - 7.0) \times 10^{-1} \text{ mol dm}^{-3}$ using NaCl, while others reaction conditions were kept constant. The effect of added Mg^{2+} and SO_4^{2-} on the reaction rate was observed by adding $(30-150) \times 10^{-3} \text{ mol dm}^{-3}$ magnesium and sulphate ion concentration respectively. While the other parameters remains constant.

RESULTS AND DISCUSSION

1:1 stoichiometric mole ratio was observed for the reaction between $[\text{CV}^+]$ and $[\text{BrO}_3^-]$ as indicated by a point of inflexion on the curve of the absorbance versus mole ratio (Figure 1)



Plots of $\log \log (A_t - A_\infty)$ versus time obtained under pseudo-first order conditions were linear for about 90% of the reactions, suggesting that the reaction is first order with respect to $[\text{CV}^+]$. Order of reaction with respect to bromate were obtained from the least square plots of $\log k_1$ versus $\log [\text{BrO}_3^-]$ as shown in Figure 2. The values of the second order rate constant, k_2 , was determined as the ratio of k_1 and $[\text{BrO}_3^-]$ were found to be fairly constant (Table 1) confirming that the reaction is first order with respect to $[\text{CV}^+]$. The rate law for the reactions can be generalized as in equation 2

$$\frac{-d[\text{CV}^+]}{dt} = k_2 [\text{CV}^+] [\text{BrO}_3^-] \quad (2)$$

Effect of Changes in Hydrogen Ions Concentration: The rate of reaction increased with increase in acid concentration (Table 1). Plot of $\log k_1$ versus $\log [\text{H}^+]$ is linear with a slope of 1.87 sec^{-1} (Figure 3). The $[\text{H}^+]$ dependent second order rate constant can thus be presented in equation 3 and is seen as a one rate term as the line passes through the origin from the plot of $k_1(\text{s}^{-1})$ against $[\text{H}^+]^2 (\text{mol}^2 \text{ dm}^{-6})$ (Figure 4)

Table 1: Pseudo-first order and second order rate constants for the reaction of CV and BrO_3^- in aqueous HCl medium, $i = 0.5 \text{ mol dm}^{-3}$, $[\text{CV}^+] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 530$ and $T = 28^\circ\text{C} \pm 1^\circ\text{C}$

$10^3 [\text{BrO}_3^-]$ mol dm^{-3}	$10^2 [\text{H}^+]$ mol dm^{-3}	$i \text{ mol dm}^{-3}$	$10^3 k_1 \text{ Sec}^{-1}$	$k_2 \text{ dm}^3$ $\text{mol}^{-1} \text{ Sec}^{-1}$
4	1	0.5	1.38	0.35
6	1	0.5	1.95	0.32
10	1	0.5	3.38	0.34
14	1	0.5	4.82	0.34
18	1	0.5	6.02	0.33
24	1	0.5	8.21	0.34
28	1	0.5	9.24	0.33
10	0.6	0.5	2.23	0.22
10	1	0.5	3.38	0.34
10	1.4	0.5	7.5	2.25
10	1.8	0.5	10.3	1.42
10	2.2	0.5	19.07	1.9
10	2.6	0.5	22.82	2.28
10	1	0.1	0.64	0.06
10	1	0.2	1.39	0.14
10	1	0.3	2.3	0.23
10	1	0.4	3.12	0.31
10	1	0.5	3.38	0.34
10	1	0.6	7.17	0.72
10	1	0.7	8.64	0.86

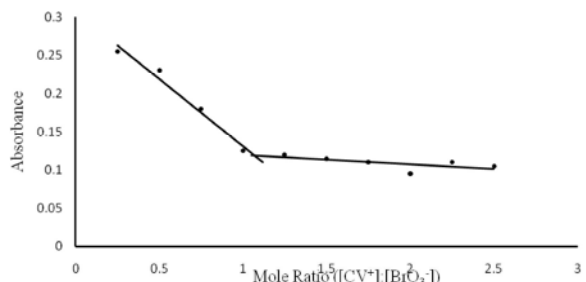


Fig. 1: Graph of absorbance against mole ratio $[\text{CV}^+]: [\text{BrO}_3^-]$

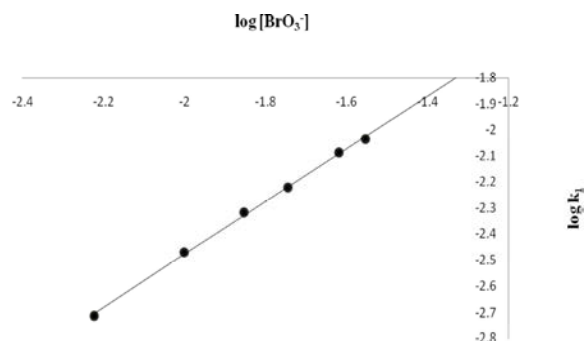
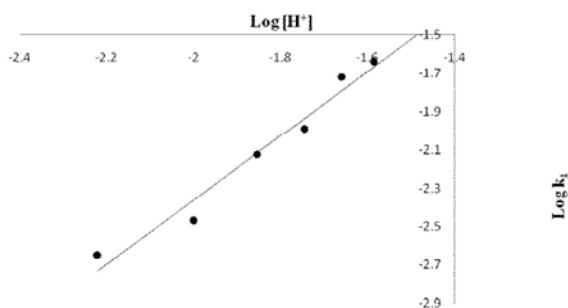
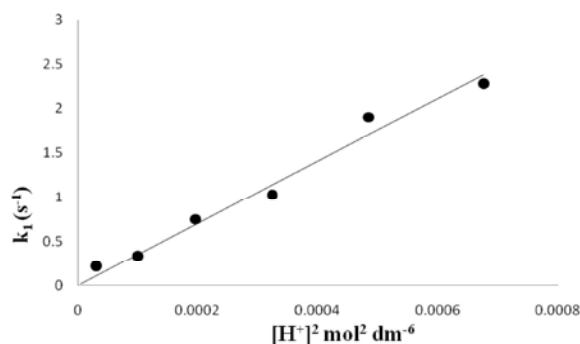


Fig. 2: Plot of $\log k_1$ versus $\log [\text{BrO}_3^-]$

$$k_1 = a[\text{H}^+]^2 \quad (3)$$

Effects of Added Ions: Added ions Mg^{2+} catalysed the reaction whereas added SO_4^{2-} inhibited the reaction. This observation suggests a possible interference caused

Fig. 3: Plot of log k_1 versus log $[H^+]$ Fig. 4: Graph of k_1 (s^{-1}) against $[H^+]^2 \text{ mol}^2 \text{ dm}^{-6}$

by the electrostatic interactions between these ions in the transition state, thereby excluding the possible formation of a binuclear intermediate in the activated complex (Table 2).

Test for Intermediate Complex: The Michealis-Menten's plot of $1/k_{\text{obs}}$ versus $1/[\text{BrO}_3^-]$ gave a straight line passing through the origin i.e. zero intercept (Figure 5), which suggests the absence of intermediate complex which is in line with literature [7].

The pseudo first order reaction of $\log (A_t - A_\infty)$ versus time were linear for about 90%. The linearity of the plot indicates that reactions are first order with respect to $[\text{CV}^+]$. Plot of $\log K_1$ versus $\log [\text{BrO}_3^-]$ gave a slope of 0.755 with correlation $R^2 = 0.970$ showing that the reaction is first order with respect to $[\text{BrO}_3^-]$.

Thus, the equation of the reaction is given as:

$$\frac{d[\text{CV}^+]}{dt} = k_1 [\text{CV}^+] [\text{BrO}_3^-] \quad (4)$$

The rate constants of the reaction were found to increase with increase in acid concentration. Plot of $\log k_1$ versus $\log [H^+]$ was linear with a slope of 1.87, an indication that the reaction is second order with respect

Table 2: Rate data for the effect of added ions (Mg^{2+} and SO_4^{2-}) on the reaction rate of CV^+ and BrO_3^- . $[\text{CV}^+] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $i = 0.50 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 530 \text{ nm}$, $T = 28.0 \pm 1^\circ\text{C}$.

Ion, mol dm^{-3}	$10^3 [\text{Ion}] \text{ mol dm}^{-3}$	$10^3, k_1 \text{ S}^{-1}$	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ S}^{-1}$
$[\text{Mg}^{2+}]$	0	3.27	0.33
	30	4.03	0.4
	50	4.42	0.44
	70	4.58	0.46
	90	5.41	0.54
	120	6.13	0.61
	150	6.28	0.63
$[\text{SO}_4^{2-}]$	0	3.23	0.32
	30	2.86	0.29
	50	2.73	0.27
	70	2.04	0.2
	90	1.63	0.16
	120	1.48	0.15
	150	1.41	0.14

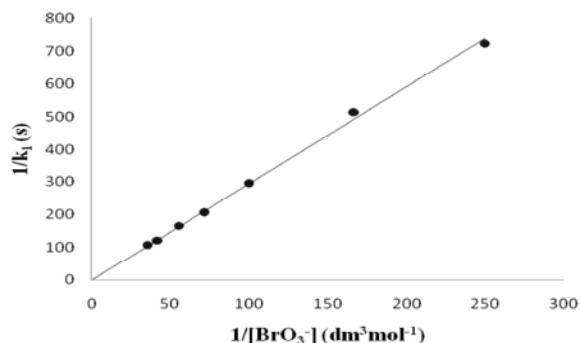


Fig. 5: Michealis-Menten's plot for the reaction of Crystal violet and bromate

to $[H^+]$. Also, the plot of k_2 versus $[H^+]^2$ passed through the origin; meaning that the reaction is a one rate term according to the equation 5:

$$K = a [H^+] \quad (5)$$

While the overall rate equation in the acid range investigated is given by the equation 6, this suggests that only the protonated forms of the reactant are reacting [8].

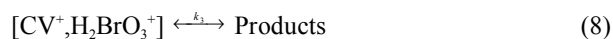
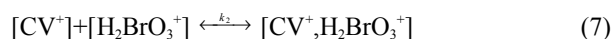
$$\frac{d[\text{CV}^+]}{dt} = a [H^+] [\text{BrO}_3^-] [\text{CV}^+] \quad (6)$$

The rate constant increases with increase in ionic strength suggesting a positive Bronsted Debye salt effect [9]. This suggest that the charge on the reactants in the activated complex is either positive-positive or negative-negative. Hence, it means species carrying the same charge sign in the activated complex are interacting [10].

The inclusion of Mg^{2+} into the reaction medium brings about increase in reaction rate while SO_4^{2-} brings about decrease in reaction rate. Both means that the reaction is catalyzed and that observation is characteristic of reactions occurring via outer sphere mechanistic pathway. This is also supported as the Michealis-Menten's plot of $\frac{1}{k_2}$ versus $1/[\text{BrO}_3^-]$ passes through the origin which is an

indication that intermediate complex is absent and the reaction system is possibly occurring through the outersphere mechanism.

Based on the results obtained in the system, the following plausible reaction mechanism has been proposed:



$$\text{Rate} = K_3 [\text{CV}^+, \text{H}_2\text{BrO}_3^+] \quad (9)$$

From equation 7

$$[\text{CV}^+, \text{H}_2\text{BrO}_3^+] = K_2 [\text{CV}^+] [\text{H}_2\text{BrO}_3^+] \quad (10)$$

Substitute equation 10 into equation 9

$$\text{Rate} = K_2 K_3 [\text{CV}^+] [\text{H}_2\text{BrO}_3^+] \quad (11)$$

From equation 6

$$[\text{H}_2\text{BrO}_3^+] = K_1 [\text{BrO}_3^-] [\text{H}^+]^2 \quad (12)$$

Substituting equation 12 into equation 11

$$\begin{aligned} \text{Rate} &= K_1 K_2 K_3 [\text{CV}^+] [\text{BrO}_3^-] [\text{H}^+]^2 \\ &= K [\text{CV}^+] [\text{BrO}_3^-] [\text{H}^+]^2 \end{aligned} \quad (13)$$

Where $K = k_1 k_2 k_3$

$$\frac{-d[\text{CV}]}{dt} = K [\text{CV}^+] [\text{BrO}_3^-] [\text{H}^+]^2 \quad (14)$$

CONCLUSION

Based on the result obtained, it is evident that stoichiometry ratio for the $\text{CV}^+ - \text{BrO}_3^-$ reaction is ratio 1:1. The reaction is first order in both $[\text{CV}^+]$ and $[\text{BrO}_3^-]$ respectively. The rates of reaction show positive dependence on changes in $[\text{H}^+]$ in the acid range used.

The positive salt effect in the reaction suggests species of like charges are reacting in the rate determining step and that activated complex is formed from common charge ions. Lack of intermediate complex formation (from Michealis - Menten's plot analysis) and catalysis due to added ions (cation and anion) is an indication that the reaction proceeded through the outer sphere mechanistic pathway.

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