



Discoloration and redox kinetics reaction of crystal violet (Gentian Violet) by $S_2O_8^{2-}$ under acidic medium

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Abstract

The kinetic of the reduction of crystal violet (CV^+) by ammonium persulphate in aqueous acidic medium has been carried out. The reaction was first order in [Oxidant] and [Reductant] with a direct proportion to the increase in $[H^+]$. The rate of the reaction decreased with increase in the dielectric constant of the reaction medium. The rate of the reaction increased with increase in ionic strength but decreased with increase in added ions. The result of spectroscopic investigation shows that there was no shift in λ_{max} which suggests that there may be no complex formation during the reaction. Fourier-transform infrared spectroscopy (FTIR) was employed in product analysis. A plausible mechanism consistent with the kinetic data has been proposed.

Keywords: Kinetics, crystal violet, rate law, ammonium persulphate, FTIR spectroscopy

Full length article *Corresponding Author, e-mail: abubakarwindia@gmail.com

1. Introduction

Crystal violet or gentian violet (also known as methyl violet 10B or hexamethyl pararosanilinechloride) is a triphenylmethane dye used as a histological stain and in Gram's method of classifying bacteria [1]. The name refers to its color, being like that of the petals of a gentian flower; it is not made from gentians or from violets. Crystal violet belongs to a class of intensely colored organic compounds called triphenylmethane dyes. The structure and color of crystal violet depend on pH [2]. The major structural form of crystal violet is the monovalent cation, abbreviated CV^+ [3]. It is used in aquaculture production due to their antibacterial, antifungal, anti-parasitic and antimicrobial [4, 5]. It is also an important group of basic dye for wools, silk and widely used to dye materials such as jute, leather, ceramics, and paper [6]. Kinetic study and mechanisms for the reactions of crystal violet with periodate and chlorate ions have been reported [7, 8].

Ammonium persulphite is an oxyanion of inorganic compound with the formula $(NH_4)_2S_2O_8$. It is a strong oxidizing agent that is used in polymer chemistry, as an etchant, and as a cleaning and bleaching agent [9, 10]. Investigation and survey of literature suggests that the discoloration and kinetic reaction of persulphate [11], fluorescent dye and Rhodamine B by persulphate ion was slow [12]. This paper would give an idea on the oxidation and reduction of crystal violet with persulphate ions and the

mechanism involve in the reaction. The idea derived would be very useful to industrial and medicinal chemist in improving its uses.

1.1. Acid, ionic strength, effect of added ions

Spectrophotometric techniques were used to determine the acid, ionic strength, and effect of added ions dependence on reaction rate. The $[CV^+]$ was kept constant while $[H^+]$ was varied in acid dependence, $[NaCl]$ was varied in ionic strength dependence, while selected cations and anions was varied in determining the effect of added ions.

2. Experimental

All chemical reagents and solvents used were analytical grade and were used without further purification. Distilled water was used throughout for all solution preparation. HCl was used to study the effect $[H^+]$ on the reaction rate, NaCl was used to maintain the ionic strength. Binary solvent of water and acetone was used to investigate the effect dielectric constant. The oxidation and reduction of crystal violet by persulphate ion was investigated using 721 visible spectrophotometer.

2.1. Stoichiometry

Spectrophotometric titration following the mole ratio method was employed in determining the

stoichiometry of the reaction. The $[CV^+]$ was kept constant while the $[S_2O_8^{2-}]$ were varied. The absorbance of the reaction mixtures was measured at 580 nm until the completion of the reaction which was indicated by a constant absorbance value. A plot of absorbance ($A_t - A_\infty$) versus mole ratio was made, from which the stoichiometry of the reaction was evaluated.

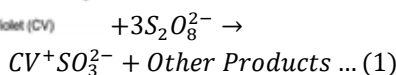
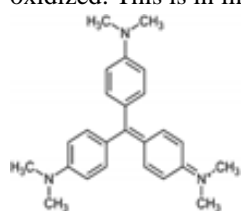
2.2. Kinetic measurement

All kinetic measurements were carried out under pseudo-first order conditions with respect to [reductant] in at least 100-folds or 1000-folds excess over that of the [oxidant] at temperature $T = 25 \pm 1^\circ C$. The ionic strength as well as the hydrogen ion concentrations of the media was maintained constant for the reaction. The rate of reaction was studied by monitoring the decrease in the absorbances of crystal violet at 580 nm.

3. Results and discussions

3.1. Stoichiometry

The result of the stoichiometric studies shows that, the mole ratio of the reaction was 1:3. This indicates that for every one mole of CV^+ , three moles of $S_2O_8^{2-}$ is being oxidized. This is in line with the equation (1):



Similar stoichiometry from literature has been reported for the oxidation of CV^+ by periodate and chlorate ions in aqueous acidic medium [7, 8].

3.2. Kinetics

3.2.1. Order of reaction

The pseudo first order plot of $\log(A_t - A_\infty)$ versus time t , was linear to about 70-80 % of the reaction (Figure 1), at constant $[H^+]$ and $[I]$. But the rate of the reaction was found to vary with increase in $[H^+]$ and $[I]$. The plot of $\log K_1$ versus $\log(S_2O_8^{2-})$ was linear with a slope of 1.2 indicate that the reaction was first order in $[S_2O_8^{2-}]$ (Figure 2). Similarly, first order reaction was reported in the study of discoloration of rhodamine with persulphate ion activation [13]. The K_2 for the reaction was found to be fairly constant (Table 1) and was obtained from $K_2 = k_1/[S_2O_8^{2-}]$, while the rate equation for the reaction can be written as

$$-\frac{d[CV^+]}{dt} = K_2[CV^+][S_2O_8^{2-}] \dots (2)$$

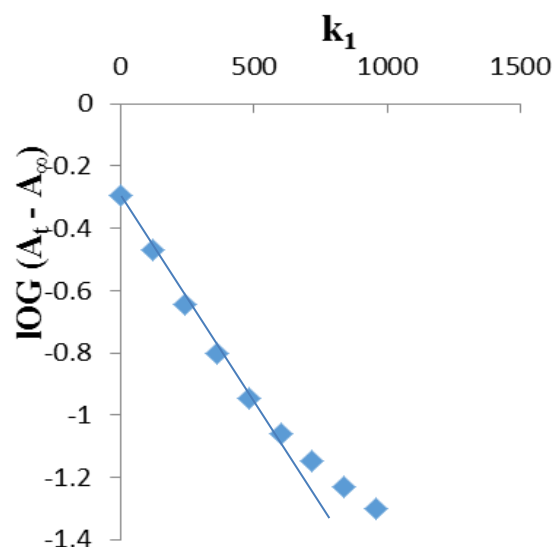


Figure 1. Typical Pseudo-first order plot for the redox reaction of CV^+ with $S_2O_8^{2-}$ at $[CV^+] = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_8^{2-}] = 1.92 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$ (NaCl), $T = 24.0 \pm 1^\circ C$ and $\lambda_{\max} = 580 \text{ nm}$

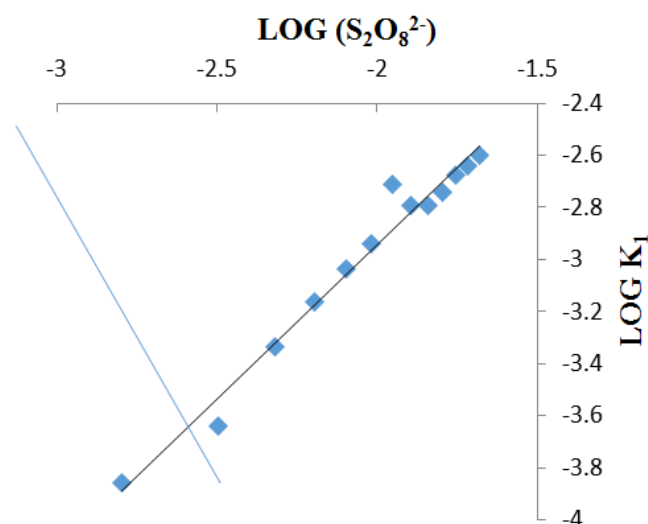


Figure 2. Plot of k_1 versus $\log[S_2O_8^{2-}]$ for the redox reaction of CV^+ with $S_2O_8^{2-}$ at $[CV^+] = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_8^{2-}] = \text{mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$ (NaCl), $T = 25 \pm 1^\circ C$ and $\lambda_{\max} = 580 \text{ nm}$

3.2.2. Effect of ionic strength

The effect of ionic strength on the reaction rates was investigated by varying the ionic strength within the range $(0.40-4.0) \times 10^{-1} \text{ mol dm}^{-3}$ while all other reactant were kept constant. The plot of $\log k_2$ versus $\sqrt{\mu}$ was linear (Figure 3). The rate of reaction was found to increase with increase in ionic strength (Table 1). This increasing effect is in agreement with the reaction of crystal violet with SO_3^{2-} [14], but a limiting effect was reported previously [15].

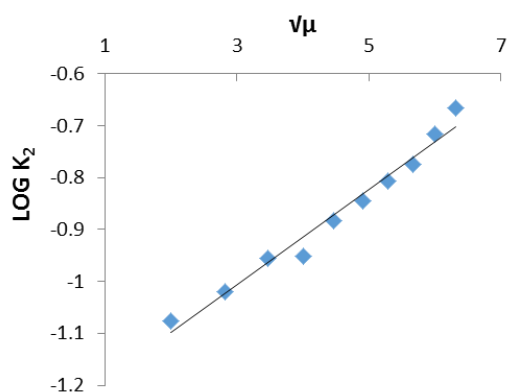


Figure 3. Plot of $\log k_2$ versus $\sqrt{\mu}$ for the redox reaction of crystal violet with persulphate ion at $[CV^+]=1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_8^{2-}]=1.92 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+]=1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu=0.4\text{-}4.0 \text{ mol dm}^{-3}$ (NaCl), $T=24 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}}=580 \text{ nm}$

3.2.3. Effect of $[H^+]$ on reaction rate

The effect of $[H^+]$ on reaction rate was studied in the range $0.4 \times 10^{-4} \leq [H^+] \leq 4.9 \times 10^{-4} \text{ mol dm}^{-3}$ while concentration CV, S_2O_8 , and μ were kept constant at 1.6×10^{-5} , 1.9×10^{-2} , and 1.0 mol dm^{-3} at $T= 25 \pm 1^\circ\text{C}$. The acid dependence rate of reaction was found to increase with increase in concentration of hydrogen ion as reported in table1. This is in consistent with the effect of $[OH^-]$ on rate constant as reported in the kinetic study of the discoloration of crystal violet ye in sodium hydroxide medium [16]. The plot of K_H versus $[H^+]$ was also linear (Figure 4), hence the acid dependent rate constant K_H is expressed by the equation.

$$-\frac{d[CV^+]}{dt} = KH[CV^+] \dots (3)$$

3.2.4. Effect of added anions

The effect of added anion was studied within the range for $[X] = 4.0 \times 10^{-2} - 2.0 \times 10^{-1} \text{ mol dm}^{-3}$ ($X= CH_3COO^-$ and NO_3^-) and concentration of $CV^+ = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $S_2O_8^{2-} = 1.92 \times 10^{-2} \text{ mol dm}^{-3}$, $H^+ = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, and $\mu = 1.0 \text{ mol dm}^{-3}$ at $T= 25 \pm 1^\circ\text{C}$. Increase in concentration of the anions $[CH_3COO^-$ and $NO_3^-]$, decreases the rate of the reaction as presented in Table 2.

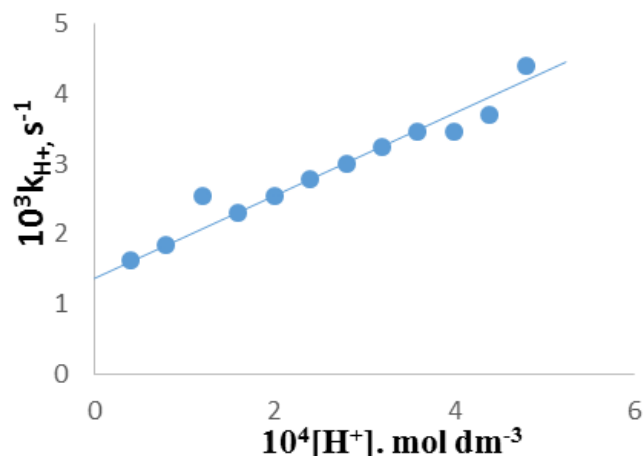


Figure 4. Plot of k_{H^+} versus $[H^+]$ for the redox reaction of CV^+ and $S_2O_8^{2-}$ at $[CV^+]=1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_8^{2-}]=1.9 \times 10^{-2}$, $[H^+]=(0.40\text{-}4.8) \times 10^{-4} \text{ mol dm}^{-3}$, $\mu=1.0 \text{ mol dm}^{-3}$ (NaCl), $T=25 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}}=580 \text{ nm}$

3.2.5. Effect of added cations

The effect of added cations was studied on the reaction rates within the range for $[Y]= 4.0 \times 10^{-2} - 2.0 \times 10^{-1} \text{ mol dm}^{-3}$, ($Y= Li^+$ and K^+) at the concentration of $CV^+ = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $S_2O_8^{2-} = 1.92 \times 10^{-2} \text{ mol dm}^{-3}$, $H^+ = 0.01 \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$ and $T= 25 \pm 1^\circ\text{C}$. Added cations were observed to catalyze the reaction. The results for these catalysis are presented in Table 2.

3.2.6. Dielectric constant effect

The effect on change in medium dielectric constant was carried out using a binary solvent (acetone and water) in the range of 5-25% at concentration for $[CV^+]= 1.6 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_8^{2-}]= 1.92 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+]= 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$ (NaCl), $\lambda_{\text{max}}= 580 \text{ nm}$ and $T=25 \pm 1^\circ\text{C}$. The effect of dielectric constant D was found to decrease the rate of reaction with decrease in dielectric constant from 78.00–55.50 (Table 3). The relationship between rate constant k_2 against $1/D$ is presented in (Figure 9).

3.2.7. Test for intermediate complex formation

The spectroscopic tests were obtained after passing the mixture of the reactant over the wave length range of 400–700 nm. The electronic spectra of the reaction which was obtained were compared with the spectra of the dye along within the same range (Figure 5). The result of the spectroscopic studies indicated no shift in absorption maxima (λ_{max}). This suggests the absence of intermediate complex during reaction.

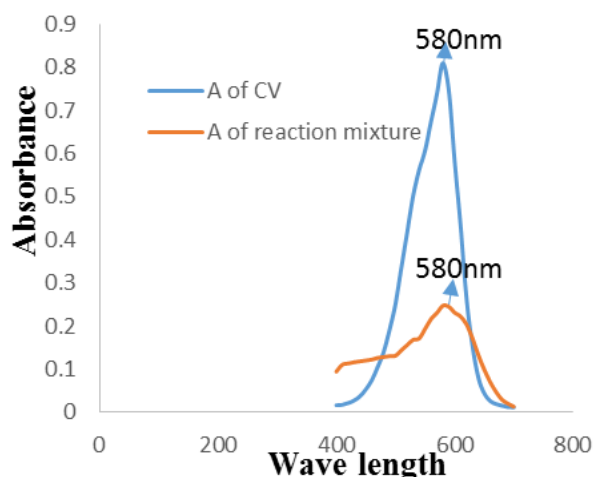


Figure 5. Spectra of the reaction mixture of CV⁺ and S₂O₈²⁻ after two minutes of reaction

3.2.8. Kinetic test (michaelis-mentens plot)

The result of the Michaelis-Mentens test was obtained. The plot 1/k₁ against 1/[S₂O₈²⁻] was found to be linear with zero or negligible intercept as in (figure 6) suggesting the absences of intermediate complex, which is in consistent with earlier reported [17].

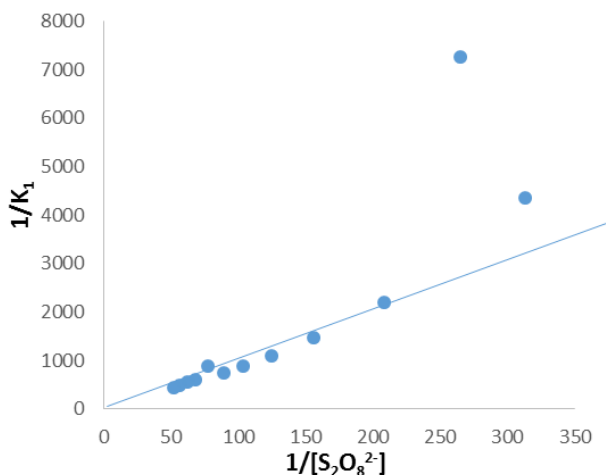


Figure 12. Michaelis-Menten plot for 1/k₁ versus 1/[S₂O₈²⁻] for the oxidation of CV⁺ by S₂O₈²⁻ at [CV⁺]=1.6×10⁻⁵ mol dm⁻³, [S₂O₈²⁻]=1.92×10⁻² mol dm⁻³, [H⁺]=0.01 mol dm⁻³, μ=1.0 mol dm⁻³ NaCl), λ_{max}=580 nm, T=25±1°C

3.2.9. Test for free radicals

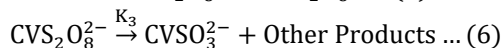
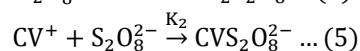
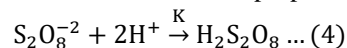
Acrylamide solution was added to the partially oxidized reaction mixture of CV and S₂O₈²⁻ ions in large excess of methanol. The mixture showed no formation of gel or precipitate, this indicated that there may be no free radical at the course of the reaction.

3.2.10. Product analysis

Product analysis was carried out by reacting [CV⁺]=1.6 × 10⁻⁵ mol dm⁻³, [S₂O₈²⁻]= 1.92 × 10⁻² mol dm⁻³, [H⁺]= 1.0 × 10⁻³ mol dm⁻³, and [I]= 1.0 molar dm⁻³ (NaCl). Spectrophotometry test indicated that there is no shift in λ_{max}, which indicated that there may not be formation of intermediate complex. Qualitative test was carried out by the addition of barium chloride solution to the product. The formation of white precipitate soluble in dilute HCl showed that SO₃²⁻ ions may be present in the products.

3.2.11. Reaction mechanism

Based on result of the above experiment, the following reaction mechanisms were proposed.



$$\text{Rate} = K_2[CV^+][S_2O_8^{2-}] \dots (7)$$

From equation 4:

$$[H_2S_2O_8] = [S_2O_8^{2-}][H^+] \dots (8)$$

Substituting equation (8) into equation (7), then obtain equation (9)

$$\text{Rate} = k_2k_1[CV^+][S_2O_8^{2-}][H^+] \dots (9)$$

Table 1. Pseudo first order and second order rate constants for the reaction of CV⁺ with S₂O₈²⁻ at [CV⁺]=1.6×10⁻⁵ mol dm⁻³, λ_{max}= 580 nm and T=24± 1°C

10³[S₂O₈²⁻] (mol. dm⁻³)	10³[H⁺] (mol. dm⁻³)	μ (mol. dm⁻³)	10⁴k₁ (s⁻¹)	10¹k₂ (dm³mol⁻¹s⁻¹)
8.0	1.0	1.0	9.21	1.15
9.6	1.0	1.0	11.5	1.19
1.12	1.0	1.0	13.8	1.23
1.28	1.0	1.0	16.1	1.25
1.44	1.0	1.0	16.1	1.11
1.60	1.0	1.0	18.1	1.22
1.76	1.0	1.0	21.0	1.19
1.92	1.0	1.0	23.0	1.19
2.0	1.0	1.0	23.5	1.17
1.92	4.0	1.0	16.1	0.85
1.92	8.0	1.0	18.3	0.96
1.92	16	1.0	23.0	1.20
1.92	20	1.0	25.3	1.31
1.92	24	1.0	27.0	1.43
1.92	28	1.0	29.9	1.56
1.92	32	1.0	32.2	1.68
1.92	36	1.0	34.5	1.80
1.92	40	1.0	34.5	1.80
1.92	1.0	4.0	1.61	0.84
1.92	1.0	8.0	1.84	0.96
1.92	1.0	1.2	2.07	1.11
1.92	1.0	1.6	2.30	1.12
1.92	1.0	2.0	2.53	1.31
1.92	1.0	2.4	2.76	1.43
1.92	1.0	2.8	2.99	1.56
1.92	1.0	3.2	3.22	1.68
1.92	1.0	3.6	3.68	1.92
1.92	1.0	4.0	4.15	2.16

Table 2. Rate of reaction for the effect of cations and anions on the first and second order rate constant for CV⁺ and S₂O₈²⁻ reaction at [CV⁺]=1.6×10⁻⁵ mol dm⁻³, [S₂O₈²⁻]=1.92×10⁻² mol dm⁻³, [H⁺]=1.0×10⁻³ mol dm⁻³, μ=1.0 mol dm⁻³, T=25±1°C and λ_{max}=580 nm

X	10 ² [X] mol dm ⁻³	10 ³ k ₁ (S ⁻¹)	10 ¹ k ₂ (dm ³ mol ⁻¹ s ⁻¹)
Li ⁺	0	2.30	1.119
	4	2.76	1.440
	8	2.99	1.559
	12	3.69	1.919
	16	4.38	2.279
	20	5.07	2.639
K ⁺	0	2.30	1.21
	4	2.76	1.44
	8	2.99	1.56
	12	3.45	1.80
	16	4.38	2.78
CH ₃ COO ⁻	0	2.53	1.32
	4	2.07	1.08
	8	1.61	0.83
	12	1.15	0.59
	16	0.69	0.34
	20	0.46	0.24
NO ₃ ⁻	0	2.53	1.30
	4	2.07	1.01
	8	1.84	0.96
	12	1.61	0.83
	16	1.38	0.72
	20	1.15	0.60

Table 3: Effect of changes in dielectric constant for the reaction of CV⁺ by S₂O₈²⁻ at [CV⁺]=1.6×10⁻⁵ mol dm⁻³, [S₂O₈²⁻]= 1.92 × 10⁻² mol dm⁻³, [H⁺]= 1.0 × 10⁻³ mol dm⁻³, μ= 1.0 mol dm⁻³ (NaCl), λ_{max}= 580 nm and T= 25± 1°C

D	10 ² 1/D	10 ³ k ₁ (s ⁻¹)	10 ² k ₂
8.40	1.28	1.61	8.40
7.20	1.33	1.38	7.20
6.00	1.39	1.15	6.00
4.80	1.45	0.92	4.80
4.00	1.82	0.69	4.00

Conclusions

The kinetic of the reduction of crystal violet (CV⁺) by ammonium persulphate in aqueous acidic medium was found to be first order in [S₂O₈²⁻]. The reaction rate was catalyzed by increase in hydrogen ion concentrations, ionic strength, added cation concentrations. The rate of the reaction decreased with increase in added anions and dielectric constant. Spectroscopic tests indicated that no intermediate complex was formed, and Michaelis-Mentens test was found to be linear with zero or negligible intercept further confirmed the absence of intermediate complex formation.

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