Chemistry Research Journal, 2019, 4(4):84-94

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Kinetics and Mechanisms of Decolorization of Crystal Violet by Cyanide ion, in Aqueous Acidic Medium

Sulaiman B. Ali[3], Osunlaja A. Adekunle[1], Fatima Y. Usman[4], Mallam W. Jibrin[2], Abubakar A. Mindia[3]

[1]Department of Chemistry, Federal University Gashua, Yobe State, Nigeria
[2]National Research Institute for Chemical Technology (NARICT) Kano State, Nigeria
[3]Department of Chemistry, University of Maiduguri, Borno State, Nigeria
[4]Department of Chemistry, Ramat Polytechnic Maiduguri, Borno State, Nigeria
* Corresponding author email: abuphauxan@gmail.com, Tel: +2348038565387

Abstract The Kinetics of the redox reaction of crystal violets (CV^+) and Cyanide ion (CN^-) in aqueous HCl has been investigated spectrophotometrically at $[H^+]$ = 2.0 x 10^{-3}mol/dm^3, μ = 0.186mol/dm^3, T = 27±1^{o}C and λ_{max}= 580nm. The reaction is first order in (oxidant: reductant) and second order overall, with stoichiometry of 1:2 (Oxidant:Reductant). The observed rate constants were not affected by changes in hydrogen ion concentration and ionic strength, but enhanced mildly with dielectric constant of the medium. Added anions and cations inhibit the reaction rate. Spectroscopic evidences suggest the absence of a stable intermediate in the course of the reaction media. Also, the activation enthalpy (ΔH* = +20.785 kJ /K/mol) and entropy (ΔS* = -180.6 J/K/mol) were determined. Plausible mechanism involving an outer-sphere complex has been proposed to explain the results.

Keywords Kinetics, Mechanism, Crystal violet, Thermodynamic, Aqueous

Introduction

Crystal violet (CV^+) is a triphenylmethane dye which has a chemical formula of ($C_{25}H_{30}N_3Cl$) it is a mixture of tetra-methyl, pentamethyl and hexamethylpararosoilins and is referred to as methyl violet 10B. It is also known as basic violet 3 and gentian violet [1]. Crystal Violet have an IUPAC name of N-(4-bis(4-dimethyl-amino)-phenyl)-methylene)-2-, 5-cyclohexadien-1-ylidine)-N-methyl-methanaminium chloride with molecular weight of 407.98 g/mol [2].

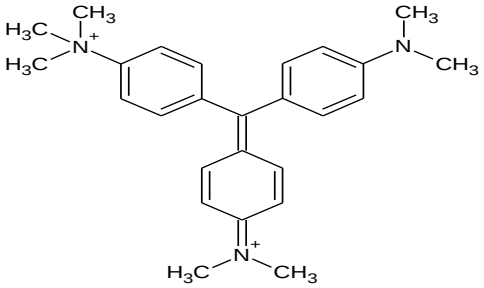

Figure 1: Structure of Crystal Violet [2].

Crystal Violet (CV^+) has various uses in textile operation, biological stain for identifying the bloody finger print being a protein dye, as a dermatological agent, and is also used in gram's stain for the demonstration and primary classification of dyes [3,4]. CV dye is medically used as an antiseptic, with a selective action on gram-positive organisms, it is also used in the treatment of burns, boils, carbuncles, and mycotic skin infection [5]. It is also used as navy blue and black inks for printing, ball-point pens, ink-jet printers, and to colourize divers' products such as fertilizers, anti-freeze, detergents and leather jackets [6].

Crystal Violet (CV^+) is considered safe for use in recommended concentrations, but in vitro it showed that the dye was a mitotic poisoning agent and it was proven in vivo studies that it is a biohazard substance [7]. Literature reveals that CV^+ when contact with eyes causes eye damage and irritation with redness and pain and when exposed to the skin causes skin damages and it is harmful if inhaled or swallowed [1]. According to [8] inhalation of CV^+ causes irritation to respiratory tract, whereas ingestion affects the gastrointestinal tract. In some extreme cases, it leads to failure of kidneys, reproductive system, liver, brain and central nervous system [9]. Due to the hazardous effect of CV^+ it has become compulsory to find an efficient and less cost effective ways of removing it from our environment by employing various wastewater removal techniques as mentioned [1].

Cyanide

There are more than 2600 plants species that exist as natural sources of cyanide including fruits and vegetables that contains cyanogenic glycosides, which can release cyanide on hydrolysis when ingested [10,11,12]. Cyanide is present in some drugs or substances which can be converted to cyanide within the body, example sodium nitroprusside ($Na_2Fe(CN)_5NO$) which is sometimes administered intravenously during the critical care treatment of hypertension, even though toxic effects of this drug was reported by [1] 0.25 ug/ml are consider normal in blood cyanide level, 0.25 and 2–3 ug/ML is considered elevated, but not ordinarily causing death, while concentrations above 3 ug/ml are consisted with death in the absence of other relevant or toxicological findings [14].

Materials and Method

Materials

All chemicals and reagents used in this work were of analytical grade and were used without further purification. NaCN was used as the reductant, single distilled water was used throughout the experiment. HCl was used to investigate the effect of hydrogen ion on the rate of reduction. NaCl being used as an inert electrolyte to maintain a constant ionic strength (μ) of the reaction medium. Methanol was used to change the dielectric constant of the reaction medium. $MgCl_2$, $CaCl_2$, Na_2NO_3, Na_2SO_4 solution were used to investigate the effects of added ions on the rate of the reaction.

Method

Stoichiometric Studies

The Stoichiometry study of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of CV^+ was kept constant and the mole ratio of cyanide ion into CV^+ was varied by keeping $[H^+]$ and ionic strength, constant at 2.0 x 10^{-3}mold/dm^3 and 0.186 mol/dm^3 respectively. The reaction was allowed to go to completion and the absorbance of the solutions monitored at 580 nm, which is a characteristics of crystal violet [15] the reaction was measured using UV Visible 721 spectrophotometer. The values obtained were plotted against the individual mole ratios of the reactants. The point of implection on the plot gave the mole ratio of the reactant.

All kinetic measurements were carried out under pseudo-first order conditions with respective CN^- concentrations with at least 100 folds excess of crystal violet concentration at temperature of 27 ± 1^0C, ionic strength 0.186 mol/dm^3 (NaCl), and $[H^+]$ = 2.0 x 10^{-3} (HCl).

The pseudo-first order plot of log (A_t - A_∞) against time were made and the slope of the plots gave pseudo-first order rate constants, k_1, the second order rate constants, k_2, were determined from k_1 as $\frac{K_1}{[CN]}$ as modified from [15].

Effect of changes in ionic strength of the reaction medium on the reaction rates was studied by varying the ionic strength from 0.106 – 0.286 mol/dm^3 (NaCl) and maintaining [CV^+], [CN^-] and [H^+] constant at 1.2 x 10^{-5} mol/dm^3, 18.0 x 10^{-2} mol/dm^3 and 2.0 x 10^{-3} mol/dm^3 respectively. Reaction temperature was maintained at 27±1 ^{0}C. Dependence of reaction rates on changes in ionic strength of reaction medium was determined by plotting log k_2 against square root of (μ).

Result and Discussion

Stoichiometry

The result of stoichiometric studies showed that one mole of CV^+ was consumed by two mole of CN^- which agrees with some literatures of stoichiometry of 1:2 reported by[16],CV^+/ ClO^-, IO_4^- , CV^+ by Ozone[17] and CV^+/ ClO_3^- [15].

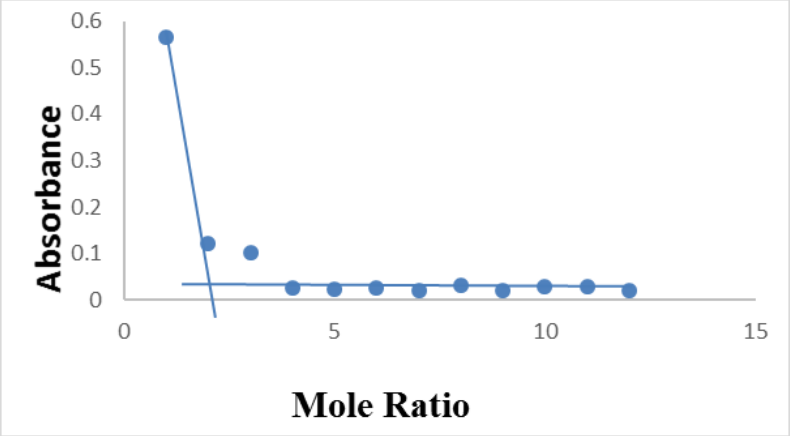

Figure 2: Plot of absorbance versus mole ratio for the determination of stoichiometry of the reduction of CV^+ by CN^- at [CV^+] = 1.2 × 10^{-5} mol dm^{-3}, [H^+] = 2.0 × 10^{-3} mol dm^{-3}, μ = 0.186 mol dm^{-3}(NaCl), T = 27.0 ± 1.0^{O}C and λ_{max} = 580 nm.

Order of Reaction

The plot of log(A_t - A_∞) versus time obtained under pseudo-first order conditions were linear for about 70% completion of the reaction. (A_t - A_∞) are the absorbance of the complex at time t and at the reaction respectively), suggesting that the reaction is first order with respect to the reactants. The slope of plot of logk_2 versus log [CN^-] was 0.9877 suggesting that the reaction is first order in [CN^-]. The derived second order rate constants, $k_1$were fairly constant, further confirming that the reaction is indeed first order in [CV^+]. This means that the reaction is second order overall and the second order rate constant determined from k_1/[CN^-] are reported in table 1. The rate law can therefore be represented by equation (1);

$$\frac{-d[CV]}{dt} = k_2[CV^+][CN^-] \quad (1)$$

The order of one in both reactants in the reaction agrees with some reported order for the redox reaction of crystal violet by BrO_3^-[17], and crystal violet $Cr_2O_7^{2-}$ [19].

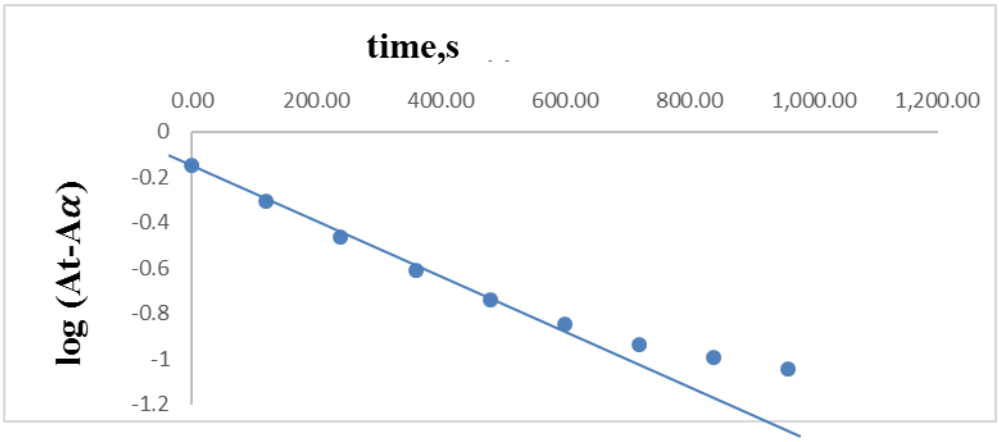

Figure 3: Pseudo-first order plot for the oxidation of CN^- by CV^+ at $[CV^+] = 1.2 \times 10^{-5}$ mol dm^{-3} $[CN^-] = 18.0 \times 10^{-3}$ mol dm^{-2}, $[H^+] = 2.0 \times 10^{-3}$ mol/dm^3, $\mu = 0.186$ mol dm^{-3} NaCl), T = 27.0± 1 ^oC and λ_{max}= 580 nm

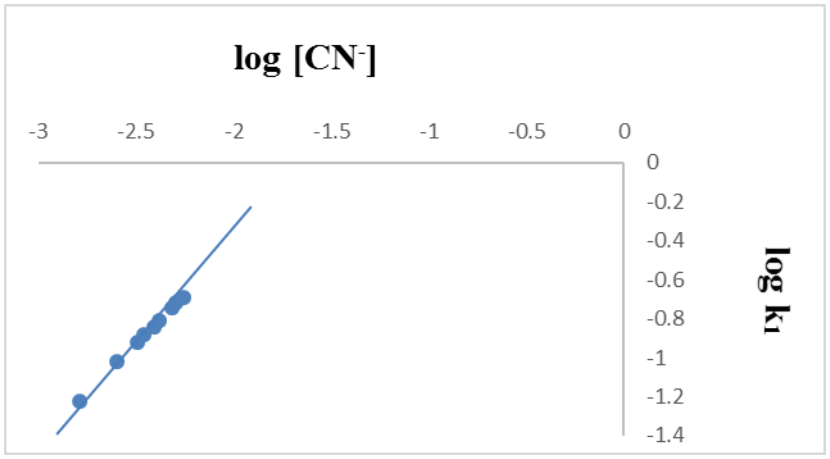

Figure 4: Plot of log k_1 versus log[CN^-] for the reaction of CV^+/CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol/dm^3 , $[H^+] = 2.0 \times 10^{-3}$ mol/dm^3, $\mu = 0.186$ mol/dm^3, T = 27±1 ^0C and λ_{max} = 580 nm.

Table 1: Pseudo-first order and second order rate constants for the reaction of CV^+ and CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol/dm^3, $\mu = 0.186$mol/dm^3, T = 27±1^{o}C and λ_{max} = 580nm

$10^2[CN^-]$mol/dm^3	$10^3[H^+]$mol/dm^3	10[μ]mol/dm^3	10^3k_1,s^{-1}	10^2k_2mol/dm^3s^{-1}
6.0	2.0	1.86	1.612	2.68
9.6	2.0	1.86	2.533	2.63
12.0	2.0	1.86	3.224	2.68
13.2	2.0	1.86	3.454	2.61
14.4	2.0	1.86	3.915	2.71
15.6	2.0	1.86	4.145	2.65
18.0	2.0	1.86	4.836	2.68
19.2	2.0	1.86	5.066	2.63
20.4	2.0	1.86	5.527	2.70
18.0	0.4	1.86	4.836	2.68
18.0	0.8	1.86	4.836	2.68
18.0	1.2	1.86	4.836	2.68
18.0	1.6	1.86	4.836	2.68
18.0	2.0	1.86	4.836	2.68
18.0	2.4	1.86	4.836	2.68
18.0	2.8	1.86	4.836	2.68
18.0	3.2	1.86	4.836	2.68

18.0	3.6	1.86	4.836	2.68
18.0	4.0	1.86	4.836	2.68
18.0	2.0	1.06	4.836	2.68
18.0	2.0	1.26	4.836	2.68
18.0	2.0	1.46	4.836	2.68
18.0	2.0	1.66	4.836	2.68
18.0	2.0	1.86	4.836	2.68
18.0	2.0	2.06	4.836	2.68
18.0	2.0	2.26	4.836	2.68
18.0	2.0	2.46	4.836	2.68
18.0	2.0	2.66	4.836	2.68
18.0	2.0	2.86	4.836	2.68

Effect of Hydrogen ion Concentration

The effect of $[H^+]$ on the rate of reaction is reported in table 1. The $k_2$values obtained from changes in hydrogen ion concentration indicated the reaction rate is not affected by these changes.

The rate law is represented by equation 2 below:

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

The average values of the second order rate constants, k_2 is (2.6868±0.06) x $10^{-2}dm^3/mol/s$. Similar results have been reported for the redox reaction of crystal violet by $S_2O_8^{2-}$ [20]. This suggests that none of the reactants is significantly protonoted under the reaction condition [15].

Effect of Changes in Ionic Strength

The increase in the ionic strength from (1.06 – 4.06) x 10^{-1} mol/dm^3 using NaCl had no effect on the reaction rate. The observed independence suggests that both charged and neutral species are reacting at the rate determining step [21].

Effect of Total Dielectric Constant

Table 2 shows the result for total dielectric constant, increased in concentration of D lead to an increase in the rate constant, Plot of log k_2 versus 1/D figure (5) showed the dependence of the second order rate constants on the dielectric constant of the reaction medium. The result suggests that outer-sphere mechanism is probably in operation, and that the reactant ions in the rate determining step are oppositely charged [22].

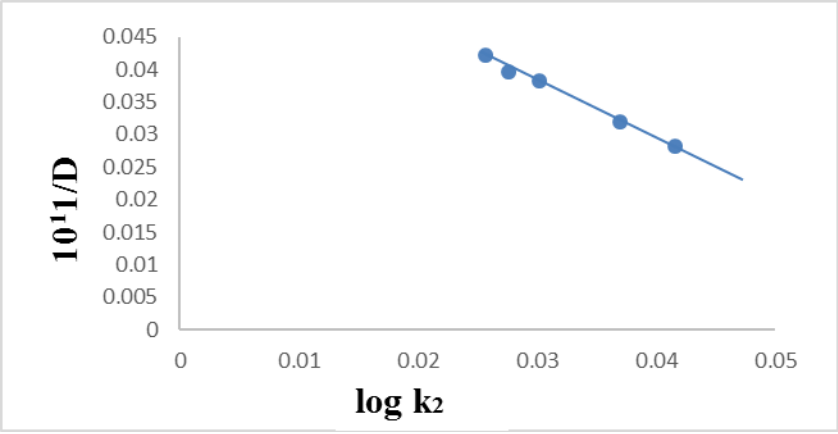

Figure 5: Plot of log k_2 against 1/D for the reduction of CV^+ by CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol dm^{-3}, $[CN^-] = 18.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.186$ mol dm^{-3}(NaCl), T = 27.0 ± 1.0^OC and λ_{max} = 580 nm

Table 2: Effect of Changes in Total Dielectric Constant of the Reaction Medium on the Reaction of Crystal Violet and Cyanide Ion [CV^+] = 1.2 x 10-5 mol/dm^3, [CN^-] = 18.0 x 10^{-7}, [H^+] = 2.0x10^{-3}mol/dm^3, μ = 0.186 mol/dm^3, T = 27±1^oC.

D	$10^2\frac{1}{D}$	10^3k_1s	$10^2k_2dm^3$/mol/s
0.00	0	4.8363	2.6868
24.03	4.1615	5.0666	2.8148
27.05	3.6968	5.7575	3.1986
30.08	3.3244	5.7878	3.3266
33.10	3.0211	6.9090	3.8383
36.21	2.7616	7.1393	3.9662
38.90	2.5705	7.5999	4.2221

Effect of Added Ions on the Rate of the Reaction

Added anions and cations Mg^+, Ca^+, SO^{2-}_4 and NO^-_3 lead to decrease in reaction rate (Table 3) and a typical plot are represented in figure 6- 9. This inhibitory effect of added ions could be explain in terms of Columbic effects, at the activated complex in this reaction is made up of positive charge species, bringing in another positively charge species would lead to overall repulsion, thereby decreasing the rate of the reaction. The effect of these ions however suggest that outer-sphere mechanism might be operating in the system [23].

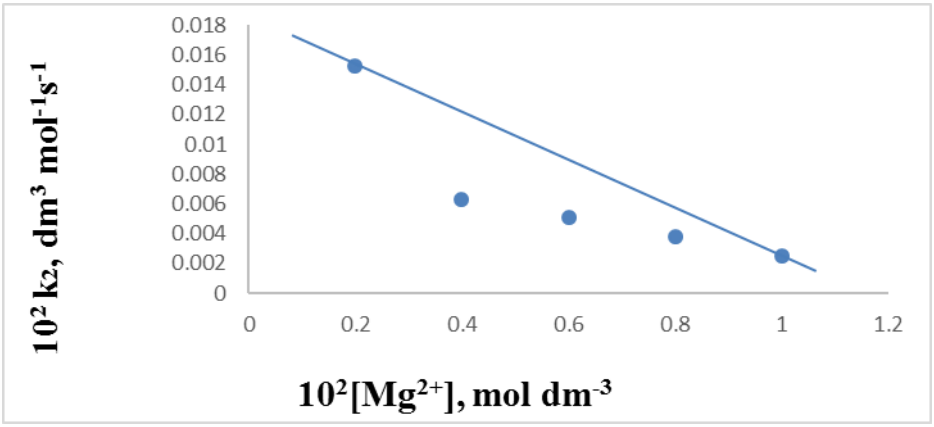

Figure 6: Plot of dependence of k_2 on [Mg^+] for the reaction of CV^+ with CN^- at [CV^+] = 1.2 × 10^{-5} mol dm^{-3}, [CN^-] = 18.0 × 10^{-2} mol dm^{-3}, [H^+] = 2.0 × 10^{-3} mol dm^{-3}, μ = 0.186 mol dm^{-3}(NaCl), λ_{max} = 580 nm and T = 27.0 ± 1.0^oC

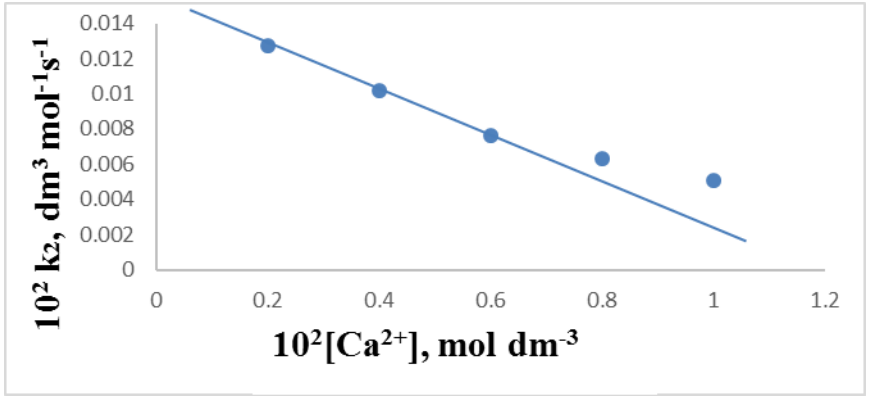

Figure 7: Plot of dependence of k_2 on [Ca^{2+}] for the reaction of CV^+ with CN^- at [CV^+] = 1.2 × 10^{-5} mol dm^{-3}, [CN^-] = 18.0 × 10^{-2} mol dm^{-3}, [H^+] = 2.0 × 10^{-3} mol dm^{-3}, μ = 0.186 mol dm^{-3}(NaCl), λ_{max} = 580 nm and T = 27.0 ± 1.0^oC

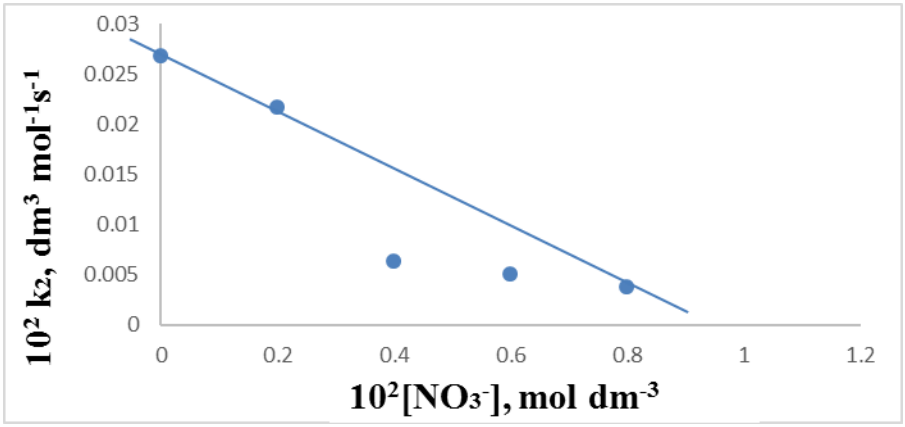

Figure 8: *Plot of dependence of k_2 on $[NO_3^-]$ for the reaction of CV^+ with CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol dm^{-3}, $[CN^-] = 18.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.186$ mol dm^{-3}(NaCl), $\lambda_{max} = 580$ nm and T = 27.0 ± 1.0^oC*

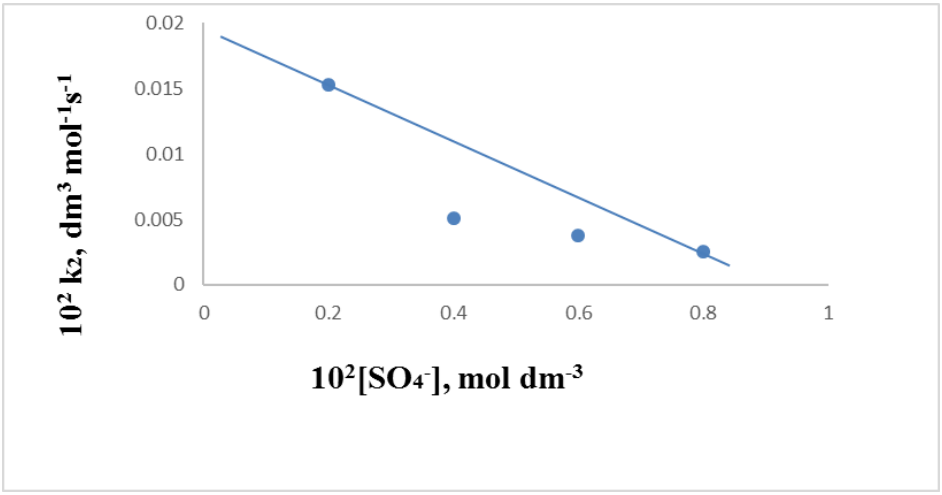

Figure 9: Plot of dependence of k_2 on $[SO_4^-]$ for the reaction of CV^+ with CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol dm^{-3}, $[CN^-] = 18.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.186$ mol dm^{-3}(NaCl), $\lambda_{max} = 580$ nm and T = 27.0 ± 1.0^oC

Table 3: Effect of Added Cations and Anions to the reaction medium on the rate constants for the oxidation of crystal violet by Cyanide ion at $[CV^+] = 1.2 \times 10^{-5}$ mol/dm^3, $\mu = 0.186$mol/dm^3, T = 27±1^{0}C, $[H^+] = 2.0 \times 10^{-3}$mol/dm^3, $\lambda_{max} = 580$nm, $[CN] = 18.0 \times 10^{-2}$mol/dm^3.

Ions	10^2[X]mol/dm3	10^3k_1s	10^2k_2dm^3/mol/s
Mg^+	0.00	4.836	2.68
	20.0	2.763	1.53
	40.0	1.151	0.63
	60.0	0.921	0.51
	80.0	0.690	0.38
	100	0.460	0.25
Ca^+	0.00	4.836	2.68
	20.0	2.303	1.27
	40.0	1.842	1.02
	60.0	1.381	0.76
	80.0	1.151	0.63
	100	0.921	0.51

NO_3^-	0.00	4.83	2.68
	20.0	2.76	1.53
	40.0	0.92	0.51
	60.0	0.69	0.38
	80.0	0.46	0.25
	100	0.263	0.12
SO_4^-	0.00	4.83	2.68
	20.0	3.91	2.17
	40.0	1.15	0.63
	60.0	0.92	0.51
	80.0	0.69	0.38

Effect of Temperature on the Reaction Rate

Increase in temperature resulted to an increase in the observed rate constants (K_{obs}). Hence, Arrhenius plot of InK_{obs} versus $\frac{1}{T}$. The entropy of activation (ΔS^*), enthalpy of activation, (ΔH^*) and gibbs free energy of activation (ΔG^*) were obtained from erying's equation as -0.1806 KJ/K /mol, 20.785 KJ/mol and 75.507 KJ/mol respectively. The result showed that an associative mechanism is operating and an endothermic reaction due the influence of some external forces.

Log K =Log A -$\frac{Ea}{2.304\,RT}$

In $(\frac{K}{T})$=$\frac{-\Delta H+}{R7}$ +in $(\frac{k1}{h})$ + $(\frac{\Delta S*}{R})$

In $(\frac{K1}{H})$= 23.76

$\Delta G^*= \Delta H^*-T\Delta S^*$

K = Observed rate constant

T = temperature

ΔH^* =enthalpy of activation

ΔS^* = entropy of activation

ΔG^* = free Gibb's energy of activation

R = molar gas constant

K^1 = Boltzmann's constant

H = plank's constant

Test for intermediate complex function

Michaeli's-menten plot of $\frac{1}{K_{obs}}$ versus $\frac{1}{CN^-}$ gave a straight line passing through the origin that is zero intercept (figure 10), suggesting the absence of intermediate complex. Also spectrum of the reaction mixture taken 2 minutes after the initiation of the reaction showed no shift from the λ_{max} of 580 nm characteristics of Crystal violet.

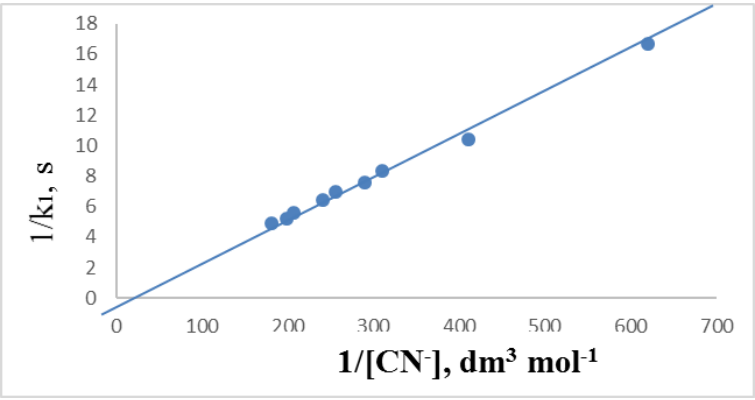

Figure 10: Michaelis-Menten plot of $1/k_1$ versus $1/[CN^-]$ for the reduction of CV^+ by CN^- at $[CV^+] = 1.2 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.186$ mol dm^{-3}(NaCl), T = 27.0 ± 1.0^OC and $\lambda_{max} = 580$ nm

Test for Participation of Free Radicals

Addition of acrylamide to the partially oxidized mixture in excess methanol did not form a gel, nor suspension and no cloud, suggesting absence of free radicals in the cause of the reaction.

Mechanisms of Reaction

Based on the results obtained, the following mechanism is proposed

$CV^+ + CN^- \xrightarrow{k1} [CV^+//CN^-]$ (3)

$[CV^+//CN^-] \xrightarrow{k2}$ Product (4)

Rate = $k_2[CV^+//CN^-]$ (5)

From equation 3

$CV^+ + CN^- \xrightarrow{k1} [CV^+//CN^-]$ (6)

Substituting (6) into (5)

Rate = $k_2k_1[CV^+][CN^-]$ (7)

If $k' = k_2k_1$, Therefore

Rate = $k'[CV^+][CN^-]$ (8)

The proposed outer-sphere mechanism pathway was as due to the following reason:

i. The rate of the reaction was inhibited in the presence of added cations and anions, this is characteristic of reactions occurring via the outer–sphere mechanism.

ii. Spectroscopic evidence indicated no shift in λ_{max} suggesting that there was absence of detectable intermediate species during the course of the reaction. This observation also suggested the outer–sphere mechanism.

iii. Michaelis - Menten plot of $1/k_1$versus $1/[CN^-]$ had zero intercept which suggests the absence of a detectable intermediate in the rate determining step. This observation suggests the occurrence of the outer-sphere mechanism.

From the above points **i – iii**, it is evident that the reaction is operating through the outer-sphere mechanism and is hereby proposed for the reaction.

Conclusion

The kinetic investigation of the redox reaction between CV^+ and cyanide ion (CN^-) were carried out in aqueous HCl medium at T = 27±1^{o}C. The reaction showed stoichiometry of 1:2. The kinetic data revealed a first order dependence on both $[CV^+]$ and $[CN^-]$ given a second order overall. Reaction rate followed acid independent pathway within the range investigated and was also not affected by increase in an ionic strength medium, but increased mildly with increase in total dielectric constant of reaction medium and inhibited by added ions. Spectrophotometric test showed absence of intermediate complex formation. This suggestion is confirmed by the evidence adduced from the Michaelis-menten plot.

Based on the above results, it is evident that the reaction is probably operating through the outer-sphere mechanism.

References

[1]. Shakila, P. B. (2018). Removal of Crystal Violet From Wastewater Using $Zncl_2$ Activated Crescentia Cujete Carbon: Adsorption Isotherm and Kinetics. *Journal Pharma Biological Science*. 9(2): 311 – 319.

[2]. Ofomaja, A. E., Ukpebor, E. E. and Uzoekwe, S. A. (2011). Biosoption of Methyl Violet onto Palm Kernel Fibre; Diffusion Studies and Multistage Process Design to Minimize Bio Sorbent Mass and Contact time. *Biomass and Bioenergy*. 33(10): 4112 – 4123.

[3]. Idrissi M., Miyah Y., Benjelloun Y., Chaouch M. (2016). Degradation of Crystal Violet by Heterogeneous Fenton-Like Reaction using Fe/Clay Catalyst with H_2O_2. *Journal of Material and Environmental Science.* 7(1), 50-58.

[4]. Bennani, K. A., Mounir, B., Hachkar, M., Bakasse, M. and Yaacoubi, A. (2017). *Journal of Material Environmental Science*, 8(3), 1082.

[5]. National Biochemicals Corporation (2015). Crystal Violet. Retrieved from http://www.national biochem.com/pdf/pis/MC3886%20PS.pdf on 20-02-2015.

[6]. Kumud, A. (2013). Removal of Dyes Using Conventional and Advanced Adsorbents. *Department of Chemical Engineering at National Institute of Technology Rourkela*, 7 – 8.

[7]. Jennifer, U. T. (2015). A Comparative Study of the Adsorption of Crystal Violet and Malachite Green from Synthetic Wastewater by Peanut and Coconut Husk Powders. *A Thesis of Department of Biochemistry University of Nigeria NSUKKA*, 1 – 26.

[8]. Hamza, M., Abdelhedi, R., Brillas, E. and Sirés I. (2009). Comparative Electrochemical Degradation of the Triphenylmethane Dye Methyl Violet with Boron Doped Diamond and Pt Anodes. *Journal Electroanal Chemistry*. 627(1–2):41–50.

[9]. Ajji, Z. and Ali, A. M. (2007). Adsorption of Methyl Violet and Brilliant Blue onto Poly (Vinyl Alcohol) Membranes Grafted with N-Vinylimidazoleacrylic acid. *Nuclear Instruments Methods B Beam Interact with Mater Atoms*. 265(1):362–365.

[10]. Ganjewala, D., Kumar, S., Devi S. A. and Ambika, K. (2010). Advances in Cyanogenic Glycoside Biosynthesis and Analysis in Plant: A Review. *Acta Biological Szeged*. 54, 1-14.

[11]. Bjarnholt, N., Rook, F., Motawia, M.S., Cornett, C., Jorgensen, C., Olsen, C.E., Jaroszewski, J. W., Bak, S. and Moller, B. L. (2008). Diversification of an Ancient Theme: *Hydroxynitrite Glcucosides. Phytochem.*, 69, 1507-1516.

[12]. Barceloux, D. G. (2008). Cyanogenic Foods (Cassava Fruit Kernels and Cyacad Seeds) in: Medical Toxicology of Natural Substances: Foods, Fungi, Medicinal Herbs, Toxic Plants and Venomous Animals. Hoboken, NJ: *John Wiley & Sons*, 44-53.

[13]. Sani, M., Sebal, H., Boughattas, N. and Ben, A. M. (2011). Time of Day Dependence of Neurological Deficits Induced by Sodium Nitropruside in Young Mice. *Journal of Circadian Rhythms.* 9, 1-8.

[14]. Gamboro, V., Arnold S., Casagni, E., Dell Acqua, L., Pecoraroch. and Faldi R. (2007). Blood Cyanide Determination in Two Cases of Fatal Intoxication: Comparison between Headspace Gas Chromatography and a Spectrophotometric Method. *Journal of Forensic Science*.52, 1401-1404.

[15]. Mohammed, Y., Etonihu, A.C. and Tsaku, V.A. (2011). Kinetics and Mechanism of Hexamethyl Pararosaniline Chloride (Crytal Violet) by Chlorate Ions in Aqueous Acidic Media. *Trakia Journal of Science.* 9(2): 1-7.

[16]. Abdulsalam, S. (2015). Kinetics and Mechanisms of the Redox Reactions of Crystal Violet with some Oxyanions in Aqueous Acidic Medium.*Unpublished M.Sc. Thesis*, Ahmadu Bello University, Zaria, Nigeria, 101-114.

[17]. Kranti, P. K. (2011). Kinetics and Mechanisms of Oxidation of Crystal Violet by Oxone. *Der Chemica Sinica* 2(6): 245-249.

[18]. Adetoro, A., Ladipo, M.K., Popoola, O.E. and Edokpayi, J.N. (2014). Electron Transfer Reaction and Mechanism of Crystal Violet with Bromate Ion in Aqueous Hydrochloric Acidic Medium. *Archives of World Journal of Chemistry*, 9(2), 20-23.

[19]. Mohammed, Y. and Komolafe, O.A. (2010). Investigations into the kinetics and mechanism of Cr (VI) oxidation of hexamethylpararosalinine chloride in aqeuous acidic medium. *Oriental Journal of Chemistry*, 26(2), 373-377.

[20]. Omotosho, M.K. (2016). Kinetics and Mechanisms of the Redox Reactions of Crystal Violet with Some Oxyanions and Hydrazine Dihydrochloride in Aqueous Medium. *An Unpublished M.Sc. Thesis*, Ahmadu Bello University, Zaria, Nigeria. 83-94.

[21]. Wilkins, G.R. (1974). The Study of Kinetics and Mechanisms of Cobalt(III)- EDTA Type Complexes. Allyn and Bacon, Inc. Boston. 231-239.

[22]. Idris, S. O., Tanimu, A., Iyun, J. F. and Mohammed, Y. (2015). Kinetics and Mechanism of Malachite Green Oxidation by Hypochlorite Ion in Aqueous Acidic Medium. *American Chemical Science Journal*. 5(2): 185-193. ISSN: 2249-0205.

[23]. Babatunde, O.A. (2005) Kinetics and mechanism of electron transfer reactions of mixed-valence di-μ-oxo tetrakis (1,10-phenanthroline) di manganese (iii,iv) ion and rosaniline hydrochloride with some reducing agents. *An unpublished Ph.D Thesis* of Ahmadu Bello University, Zaria, Nigeria.