International Journal of Sciences: Basic and Applied Research (IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

Oxidation of Cyanide Ion by 3,7 bis (dimethylamino) phenothionium Chloride in Aqueous Perchloric Acid

Babatunde O. A.[a*], Umoru Patricia Ese[b]

[ab]Department of Chemistry, Nigerian Defence Academy, P.M.B 2109, Kaduna, Nigeria
[b]Email: patriciaumoru@yahoo.com

Abstract

Oxidation of cyanide ion by 3,7-bis (dimethylamino) phenothionium Chloride in aqueous perchloric acid has been investigated at a temperature, T= 30 ± 1°C, $[H^+] = 1 \times 10^{-3}$ mol dm^{-3} and ionic strength, I= 1.0 mol dm^{-3}. The reduction is first order in both oxidant and reductant. The rate of reaction was found to decrease with increase in ionic strength concentration and increased with increase in dielectric constant concentration; added anion and cation did not have any effect on the rate of reaction. The reaction rate showed inverse $[H^+]$ dependence and obeyed the rate law:

$$\frac{-d\,[MB^+]}{dt} = a + b[H^+]^{-1}[MB^+]\,[CN^-]$$

at 30 ± 1°C, $[H^+] = 1 \times 10^{-3}$, 1.0 mol dm^{-3} ($NaClO_4$) ionic strength and $\lambda_{max} = 663$ nm. Investigation of spectroscopic test did not indicate the formation of intermediate complex of significant stability and free radicals are absent. Added anion did not have any observable effect on the rate of reaction therefore, the mechanism of reaction is proposed in terms of outer-sphere mechanism.

Keywords: Kinetics; Oxidation; Mechainsm; 3,7-bis (dimethylamino) phenothionium Chloride; Cyanide ion;

---

* Corresponding author.

E-mail address: patriciaumoru@yahoo.com.

1. Introduction

3,7-bis (dimethylamino) phenothionium chloride (herein referred to as MB^+), is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$ and belongs to the phenothiazine group. At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water. 3,7-bis (dimethylamino) phenothionium chloride and light have been known to have virucidal properties for over 80 years according to Wagner [1]. 3,7-bis (dimethylamino) phenothionium chloride have been found very useful by cardiac surgical teams in the treatment of extremely low blood pressure (hypotension) which may occur during heart surgery requiring cardiac bypass. Similar use is noted in the treatment of hypotension associated with overwhelming infections (sepsis). The 3,7-bis (dimethylamino) phenothionium chloride is also important to soil microbiologist to quickly detect in water the metabolic activity of sulfate reducing bacteria (SRB) [2]. Furthermore, 3,7-bis (dimethylamino) phenothionium chloride was also used in the mid-twentieth century in the treatment of carbon monoxide poisoning also large doses of 3,7-bis (dimethylamino) phenothionium Chloride are sometimes used as antidote to potassium cyanide poisoning according to Matilda [3] in San Francisco.

Cyanide is widely used in organic synthesis for the preparation of nitriles and carboxylic acids [4]**.** It is also used for the mining of gold and silver: it helps dissolve these metals and their ores. Similarly, the cyanide compound sodium nitro-prusside is used mainly in clinical chemistry to measure urine ketone bodies mainly as a follow-up to diabetic patients. On many occasion, it is used in emergency medical situations to produce a rapid decrease of blood pressure in humans. During World War I, a copper cyanide compound was briefly used by Japanese physicians for the treatment of tuberculosis and leprosy [5]. It has also found use in the killing of native birds, including the endangered kiwi [6].

The reaction has been studied in order to give an insight to the mechanism of the reaction and also be a useful tool in improving on the uses of 3,7-bis (dimethylamino) phenothionium chloride and cyanide ion.

1.1 Materials and Methods

Analytical grade reagents from BDH Chemical Company England were used without further purification throughout this work. All solutions were prepared with distilled water. Perchloric acid ($HClO_4$) and sodium perchlorate ($NaClO_4$) were used to investigate the effect of hydrogen ion concentration and ionic strength of the reaction medium respectively.

1.2 Stoichiometric Studies

The stoichiometries of the reactions were determined by spectrophotometric titration, using the mole ratio method. In all the systems, the concentrations of the 3,7-bis (dimethylamino) phenothionium chloride were kept constant while that of cyanide ion was varied. $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} and $T = 30 \pm 1^{o}C$ and $\lambda_{max} = 663$ nm. The reacting mixtures were allowed to stand for 24 hours until the reaction has gone to completion, when the absorbance had attained a steady value. The final absorbances were taken and the graphs of absorbance against concentration were plotted, the stoichiometries were then evaluated from the point of inflection on the graphs.

1.3 Kinetic Measurements

The rates of depletion in the concentration of the reactants were followed by monitoring the decrease in the absorbance of 3,7-bis (dimethylamino) phenothionium chloride at a specific wavelength of 663 nm using UV/Vis Spectrumlab 752s spectrophotometer. All kinetic measurements were performed under pseudo-first order conditions with the concentration of the MB^+ kept constant and that of cyanide ion maintained at least 20 – fold excess over that of the oxidant. $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} and T = 30 ± 1°C and $\lambda_{max} = 663$ nm.

1.4 Effect of Change in Hydrogen Ion Concentration on Rate of Reaction

The influence of hydrogen ion concentration on the rate of the reactions were studied by keeping the concentration of all other parameters constant while that of the perchloric acid were varied at $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} and T = 30 ± 1°C and $\lambda_{max} = 663$ nm. Graph of k_2 versus $[H^+]$ was plotted.

1.5 Effect of Change in Ionic Strength on Reaction Rate

The influence of ionic strength on the rate of the reaction was studied by keeping the concentration of all other parameters constant while that of the sodium perchlorate were varied using $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} and T = 30 ± 1°C and $\lambda_{max} = 663$ nm. Graph of log k_1 versus $\sqrt{1}$ was plotted.

1.6 Effect of Change in Dielectric Constant on Rate of Reaction

The effect of changes in the dielectric constant of the reaction medium on the reaction rate were investigated by adding acetone in a range of 0.5-1.4 % to the reaction mixture, while keeping other parameters constant. $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} and T = 30 ± 1°C and $\lambda_{max} = 663$ nm.

1.7 Effect of Added Ions on Rate of Reaction

The effect of added ions on the reaction rate were studied by adding 0.2 - 3.5 x 10^{-3} of ions (CH_3OO^- and Li^{2+}) to the reaction mixture while keeping other parameters constants.

1.8 Test for Intermediate Complex

a. Spectroscopic Test: The electronic spectra of the reaction mixtures were run after every five minutes after the commencement of the reaction. These were compared with the spectra of the dye alone over a wavelength range of 550 – 700 nm.

b. Michaelis-Mentens plots of $1/k_1$ versus 1/Reductants were made.

1.9Test for Free Radicals

A solution of 2 cm^3 of acrylamide was added to the partially oxidized reaction mixture containing various concentrations of oxidants, reductants and hydrogen ion, followed by large excess of methanol to initiate free radical polymerization. Acrylamide was also added to each of the reactants separately to serve as control.

1.10 Product(s) Analysis

After the completion of the reaction system, identified by the formation of colourless solutions, IR spectra was carried out on the colourless solution to identify the functional group of the compound present.

2. Results and Discussion

2.1 Stoichiometry

The result for stoichiometry showed that 1 mole of MB+ is consumed by 1 mole of CN^-. This is in good agreement with what was obtained by [7] for MB^+/1, 3-dimethyl-2-thiourea, also MB^+/thiourea by [8] mercaptoaceticacid and L- ascorbic acid by [9] and MB^+/thiosulphate [10]. The rate equation is given as:

$$MB^+ + CN^- \longrightarrow \text{products} \qquad 1$$

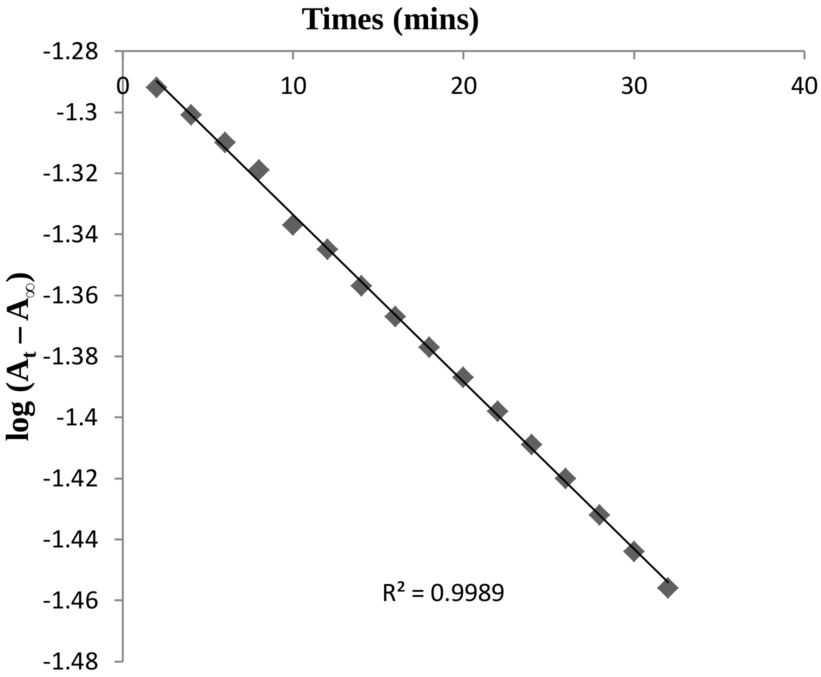

Figure 1: A typical pseudo-first Order Plot for the Reaction of Methylene Blue with Cyanide Ion. $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3} and T = 30 ± 1°C and $\lambda_{max} = 663$ nm.

2.2 Kinetics Studies

Plots of log ($A_t - A_\infty$) versus time (mins) were linear to about 90 % extent for the reaction system indicating a first order dependence of rate on [MB^+] (fig. 1). This is consistent with the results reported by many authors in reactions of MB^+/1, 3-dimethyl-2-thiourea by [7]; MB^+/bromate ion by [11]; MB^+/β-Mercaptoethanol by [10].

The plot of log k_1 (where k_1 is the pseudo-first order rate constant) versus log [reductant] at constant [H^+] was also linear and suggest a first order rate constant with respect to the concentrations of CN^- (fig. 2). Ethylenediaminetyltraacetomanganate (III)/CN^- by [12] respectively. Second order rate constant, k_2, were obtained from $k_2 = k_1$/[reductant] and were found to be fairly constant (Table 1). The overall order for the system is second order with rate law written as:

$$\frac{-d[MB+]}{dt} = k_2[MB^+][CN^-] \qquad 2$$

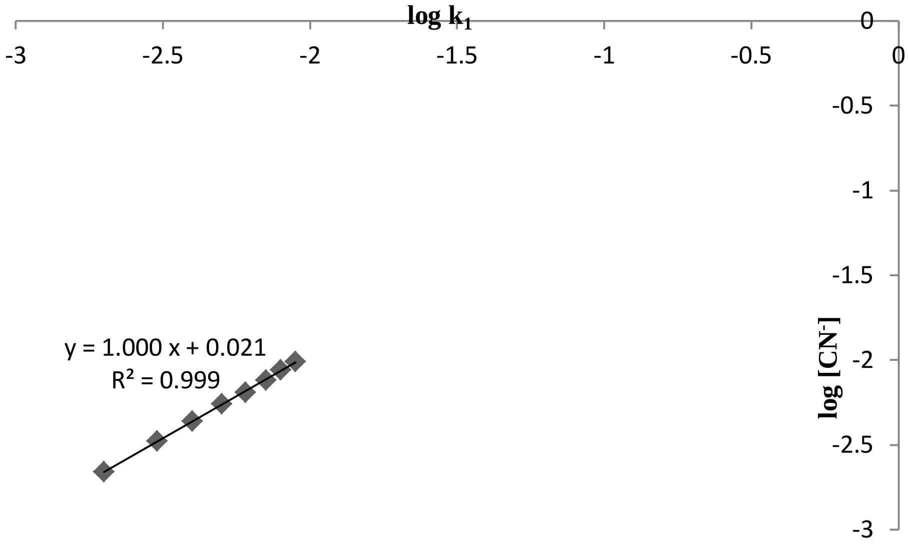

Figure 2: Plot of log k_1 vs log [CN^-] for the Reaction of Methylene Blue and Cyanide Ion. [MB^+] = 1.0 x 10^{-4} mol dm^{-3}, [H^+] = 1.0 x 10^{-3} mol dm^{-3}, I = 1.0 mol $dm^{-3}$and 30 ± 1°C and λ_{max} = 663 nm.

2.3 Effect of Change in Hydrogen Ion Concentration

Changes in [H^+] affected the rate of reaction inversely in the acid range used $0.5 \times 10^{-3} \leq [H^+] \leq 4.0 \times 10^{-3}$ mol dm^{-3} (Table 1). Decrease in rate of reaction with increase in [H^+] had been explained in terms of the de-protonation of one of the reactant prior to electron transfer [13]. A plot of acid-dependent second order rate constant, k_H^+, against [H^+] was linear with a slope = -0.479 dm^3 mol^{-1} min^{-1} and intercept of 3.20 dm^3 mol^{-1} s^{-1} (Fig. 3), suggesting that this reaction occurs by two parallel pathways. One of the pathways is inverse acid-dependent and the other acid - independent. This result obeys the equation:

$$k_H^+ = a + b[H^+]^{-1} \qquad 3$$

The rate equation for the reaction of methylene blue and cyanide ion can now be written as:

$$-\frac{d}{dt}[MB^+] = (a + b[H^+]^{-1}[MB^+][CN^-] \qquad 4$$

where a = 3.203 $dm^3\ mol^{-1}\ min^{-1}$, b = -0.479 $dm^6\ mol^{-2}\ min^{-1}$

Table 1: Pseudo-first Order Rate Constant for the Reaction of $MB^+ = 1x\ 10^{-4}$ by CN^- at 30 ± 1°C, I $[NaClO_4^-]$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol $dm^{-3}$and λ_{max} = 663 nm.

$10^3\ [CN^-]$ mol dm^{-3}	**I $[NaClO_4^-]$mol dm^{-3}**	**$[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}**	**$10^3\ k_1 min^{-1}$**	**$k_2\ dm^3\ mol^{-1}\ min^{-1}$**
2.0	1.0	1.0	5.69	2.84
3.0	1.0	1.0	8.50	2.83
4.0	1.0	1.0	11.31	2.84
5.0	1.0	1.0	14.28	2.86
6.0	1.0	1.0	16.90	2.82
7.0	1.0	1.0	19.92	2.85
8.0	1.0	1.0	22.91	2.84
3.0	1.0	0.5	9.00	3.00
3.0	1.0	1.0	8.41	2.82
3.0	1.0	1.5	7.23	2.41
3.0	1.0	2.0	6.53	2.19
3.0	1.0	2.5	5.85	1.95
3.0	1.0	3.0	5.19	1.72
3.0	1.0	3.5	4.65	1.55
3.0	1.0	4.0	4.08	1.36
3.0	0.5	1.0	10.02	3.34
3.0	1.0	1.0	8.57	2.86
3.0	1.5	1.0	7.58	2.53
3.0	2.0	1.0	6.77	2.26
3.0	2.5	1.0	5.80	1.93
3.0	3.0	1.0	5.50	1.83
3.0	3.5	1.0	4.81	1.60
3.0	4.0	1.0	4.44	1.48

2.4 Effect of Ionic Strength

The plot of log k_1 against $\sqrt{I}$ was made and this gave a straight line with a negative slope of -0.276 (Figure 4). A negative salt effect was observed in the redox reaction as the rate of reaction was found to decrease with increase in ionic strength of the reaction medium from $0.5 \leq I \leq 3.5$ mol dm^{-3}. The observed slope of less than one suggests that there is the possibility that there was no bond formation at the transition state and the reaction involves two opposite charges.

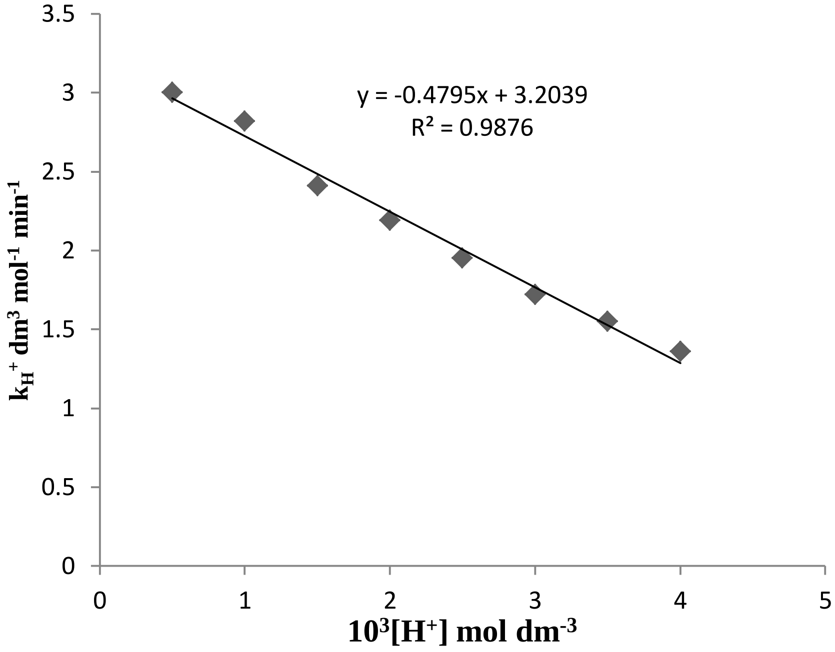

Figure 3: Plot of k_{H^+} vs **[**H^+] for the Reaction of Methylene blue and Cyanide Ion. [MB^+] = 1.0 x 10^{-4} mol dm^{-3}, [CN^-] = 3.0 x 10^{-3} mol dm^{-3}, [H^+] = 1.0 x 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3}and 30 ± 1°C and λ_{max} = 663 nm.

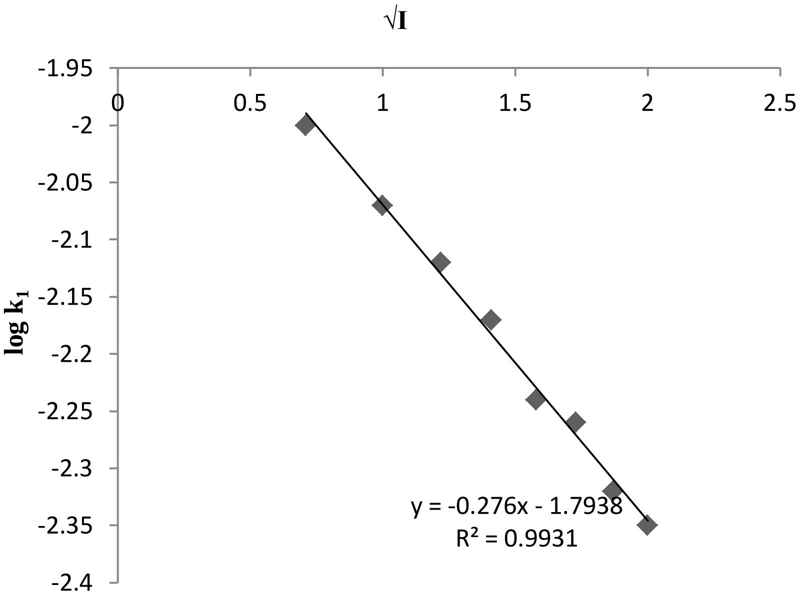

Figure 4: Plot of log k_1 vs √I for the Reaction of Methylene Blue and Cyanide Ion. [MB^+] = 1.0 x 10^{-4} mol dm^{-3}, [CN^-] = 3.0 x 10^{-3} mol dm^{-3}, [H^+] = 1.0 x 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3}and 30 ± 1°C and λ_{max} = 663 nm.

2.5 Effect of Dielectric Constant

Increase in the concentration of acetone increased rate of reaction for effect of dielectric constant.

Table 2: Effect of Changes in Total Dielectric Constant.

D	**1/D**	**$10^3 k_1 s^{-1}$**	**$k_2 dm^3 mol^{-1} s^{-1}$**
0.2	5.0	3.22	0.81
0.4	2.5	4.61	1.15
0.6	1.67	5.23	1.31
0.8	1.25	6.45	1.61
1.0	1.00	7.77	1.94
1.2	0.83	9.15	2.29
1.4	0.71	10.74	2.68

$[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[CN^-] = 3.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3}, 30 ± 1ºCand λ_{max} = 663 nm

Table 3: Effect of Added Cation and Anion

Ions	**10^3[Ion] mol dm^{-3}**	**$10^3 k_1 min^{-1}$**	**$k_2 dm^3 mol^{-1} min^{-1}$**
Li^{2+}			
	0.5	2.30	5.76
	1.0	2.30	5.76
	1.5	2.30	5.76
	2.0	2.30	5.76
	2.5	2.30	5.76
	3.0	2.30	5.76
	3.5	2.30	5.76
CH_3OO^-			
	0.2	2.76	6.90
	0.4	2.76	6.90
	0.6	2.76	6.90
	0.8	2.76	6.90
	1.0	2.76	6.90
	1.2	2.76	6.90
	1.4	2.76	6.90

$[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[CN^-] = 3.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 1.0 mol dm^{-3}, 30 ± 1ºC and λ_{max} = 663 nm

Effect of Added Cation and Anion

Lithium and CH_3OO^- ions did not show any effect on the rate of reaction (Table 3).

2.6 Test for Presence of Free Radicals

Acrylamide solution (2 cm^{-3}) was added to the partially reacted mixture but did not form a gel even in the presence of excess methanol indicative of the absence of free radical.

2.7 Spectroscopic Analysis

The plot of $1/k_1$vs $1/[CN^-]$ gave no intercept indicating a precursor complex was probably not formed prior to electron transfer (Fig. 5).

2.9 Product Analysis

The product of the reaction was identified from an IR spectrum at 2073.55 cm^{-1} indicating the presence of nitrile compound.

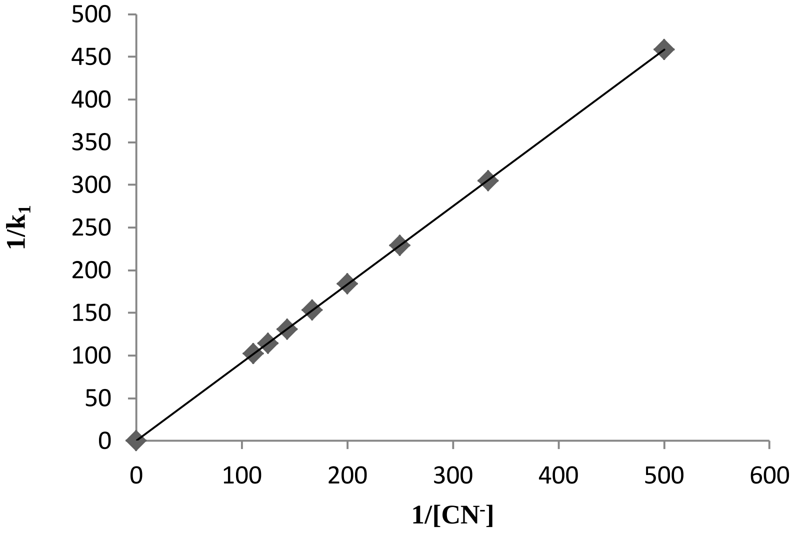

Figure 5: Michaelis-Menten's Plot of $1/k_1$ vs $1/[CN^-]$. $[MB^+] = 1.0 \times 10^{-4}$ mol dm^{-3}. $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-1}, I = 1.0 mol $dm^{-3}$and 30 ± 1°C and $\lambda_{max} = 663$ nm.

3. Reaction Mechanism

$$MB^+ + CN^- \overset{K_{eq}}{\rightleftharpoons} [MB - CN] \qquad 5$$

$$[MB - CN] \xrightarrow[H_2O\ slow]{k_1} product \qquad 6$$

From equation 6

$$\text{Rate} = k_1[MB - CN] \qquad 7$$

$$\text{but } [MB - CN] = K_{eq}\frac{[MB^+][CN^-]}{[H^+]} \qquad 8$$

$$\text{Rate} = \frac{k_1K_{eq}[MB^+][CN^-]}{[H^+]} \qquad 9$$

If $k_1K_{eq} = a + b$

$$\text{Rate} = a + b[H^+]^{-1}[MB^+][CN^-] \qquad 10$$

The following points where considered in order to assign a plausible mechanism of reaction:

Absence of free radicals in the reaction mixture suggests an outer-sphere.

The Michaelis- Menten plot of $1/k_1$vs $1/[CN^-]$ was linear without an intercept indicating the absence of intermediate complex formation. This suggests the outer-sphere mechanism [14].

Absence of spectrophotometric evidence of intermediate complex formation suggests that an intermediate complex was probably not formed prior to electron transfer and redox reaction occurs by outer-sphere mechanism.

It is therefore evident from the above that the reaction of MB^+ with cyanide ion most probably occurred by the outer-sphere mechanism.

4. Conclusion

In conclusion, this reaction indicates a second order rate law and has an inverse hydrogen ion dependent on rate of reaction. Also scanning of the reaction mixture did not show any shift in λ_{max} pointing to the absence of formation of intermediate complex and absence of free radical formation during the reaction. All these points above are in support of the outer sphere mechanism. Therefore, the reaction occurs probably by outer sphere mechanism.

References

[1] S. J. Wagner, A. Skripchenko, D. Robinette , D. A. Mallory, J. Hirayama, L. Cincotta and J. Foley, (2000). "The use of dimethylmethylene blue for virus photoinactivation of red cell suspensions". *Dev Biol (Basel)* vol. 102 pp. 125–9,

[2] J. R. Olliver, C. P. Wild, P. Sahay, S. Dexter, L. J. Hardie, (2003). "Chromoendoscopy with methylene blue and associated DNA damage in Barrett's oesophagus". *Lancet* vol. 362, pp. 373–4.

[3] M. B . Matilda, (1936). “Methylene Blue as an Antidote for Cyanide and Carbon Monoxide Poisoning”. *The*

Scientific Monthly, vol. 43 pp. 585–586.

[4] H.T. Stokes, D.L. Decker, H.M. Nelson, and J. D. Jorgensen, (1993).”Structure of potassium cyanide at low temperature and high pressure determined by neutron diffraction”. *Physical Review B* vol. 47 pp. 11082–11092,

[5] Z. Takano. (1916). “The Treatment Of Leprosy With Cyanocuprol”. *The Journal of Experimental Medicine* 24 Vol. 2 pp. 207–211.

[6] W. Green, (2004). “The use of 1080 for pest control”. New Zealand Department of Conservation.

[7] A. A. Osunlaja, S.O. Idris, J.F. Iyun, and A. Uzairu, (2013). “Oxidation Of 1, 3-Dimethyl-2-Thiourea By 3, 7-Bis(Dimethylamino)Phenazothionium Chloride In Aqueous Hydrochloric Acid” *International Journal of Pharmaceutical, Chemical and Biological* Vol. 3 pp. 861-869.

[8] A. A. Osunlaja, S.O. Idris, and J.F. Iyun. (2012). “Kinetics and Mechanisms of the Methylene blue – permanganate Ion in Acidic Medium’’ *International Journal of ChemTech Research* , Vol. 4 Pp 772-780.

[9] B. M. Bugaje, (2006). “Kinetics and mechanisms of redox reactions of methylene blue and ethylenediamine tetracetatocobaltate(II) with some oxy-anions in aqueous solution’’ M.Sc.thesis. Chemistry Department, Ahmadu Bello University, Zaria.

[10] P. O. Ukoha, (2005). “Kinetics and mechanisms of the reduction of 3,7-bis(dimethylamino) phenazothionium chloride by β-mercaptoethanol in acid media”. *.J. Chem. Soc. Nigeria.* Vol. 30 pp. 165-170.

[11] J.F. Iyun, and M. Asala. (1994). “Mechanism of bromate oxidation of 3,7-bis (dimethylamino)phenazothionium chloride’’ A paper presented at the 18th annual conference of the chemical society of Nigeria, Kano. 29th May – 2nd June.

[13] T.S. Zueva, E. V. Protopopov and I.A Ivanov. (1969). “Role of thiols (Cysteine and Thiourea) in the mechanism of the periodic decomposition reaction of hydrogen peroxide by potassium iodate in acid medium”. *TERCAXA.* Vol. 26 pp. 51-56.

[14] T.T. Przystas, and N. Sutin. (1973). “Kinetics Studies of Anion – Assisted outer-sphere Electron Transfer Reactions’’ *J. Amer. chem soc,* Vol. 95 pp. 5545.