



# Kinetics of Redox Reaction between Malachite Green and Hydroxyl Ion

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## ABSTRACT

Kinetics investigation of redox reaction between malachite green,  $MG^+$  and hydroxyl ion was carried out in aqueous medium at  $22 \pm 1^\circ C$  at ionic strength =  $0.5 \text{ mol dm}^{-3}$ . The reaction is first order with respect to both  $MG^+$  and  $OH^-$  having the empirical rate law:

$$-d[MG^+]/dt = k_2[MG^+][OH^-]$$

$$\text{Where } k_2 = 47.36 \pm 0.14 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

The reaction displays a negative salt effect and the reaction rate decreases with increasing anion concentration. A plausible mechanism is proposed for the reaction based on the results obtained.

**Keywords:** Kinetics, Mechanism, Malachite Green, Hydroxyl ion, Outer-sphere

## 1. INTRODUCTION

Malachite green also called aniline, basic green 4, diamond green or Victoria green B is a triphenyl methane dye and a derivative of bis(p-aminophenyl) phenyl methane. Literature has shown that it has a wide range of applications. For example, it is used to dye materials like silk, leather and paper [1,2]. The dye has a powerful antiseptic property against wide spectrum of microbes [2,3,4]. In spite of these and other numerous uses of this compound [5,6], kinetic investigation on its reaction is scanty. In this report, we present kinetic investigation of electron transfer reaction between malachite green and hydroxyl ion with the aim of gaining an insight into the mechanism of their reaction.

## 2. EXPERIMENTAL

Malachite green, microscopy grade (Thomas Baker) here and thereafter referred to as  $MG^+$  was used without further purification. All the reagents used were analytical grades except otherwise stated. A stock solution of sodium hydroxide was prepared and standardized titrimetrically against standard solution of succinic acid. Standard solution of sodium chloride is used to keep ionic strength of reaction medium constant while standard solution of sodium nitrate, sodium acetate and sodium sulphate were used to probe the effect of anions on the reaction rate.

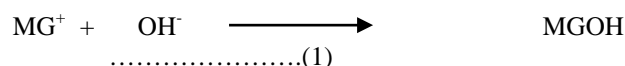
Changes in absorbances were monitored on Corning Colorimeter 253. Kinetic measurements were conducted by monitoring decrease in absorbance of the  $MG^+$  at 620nm. All measurement was carried out under

pseudo-first order condition with  $[OH^-]$  in at least 100-fold excess over  $[MG^+]$  at  $0.5 \text{ mol dm}^{-3}$  (ionic strength of reaction medium).

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [7].  $MG^+$  concentration was kept at  $1 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 22^\circ C$  and  $[OH^-] = 4 \times 10^{-5} - 40 \times 10^{-6} \text{ mol dm}^{-3}$ . A point of inflexion on the curve of absorbances at infinity versus mole ratio corresponds to the reaction stoichiometry.

## 3. RESULTS AND DISCUSSION

The 1:1 stoichiometry indicated by the results of spectrophotometric titration (fig.3) suggests that the overall reaction can be represented by equation (1)



This is in agreement with what has been reported for some of the reactions of  $MG^+$  [8, 9]

## 4. KINETIC STUDIES

The pseudo-first order plots of  $\log (A_\infty - A_t)$  versus time for these reactions were linear for over 95% extent of reaction. This suggests that there is no product inhibition and that the reaction is first order in  $[MG^+]$ . The observed pseudo-first order rate constants,  $k_{obs}$  were obtained from the slopes of the above plots as given by equation 2.

$$\log (A_\infty - A_t) = A_\infty - A_0 e^{-k_{obs}t}$$

.....(2)



where  $A_{\infty}$  and  $A_t$  are the absorbances at the end of reaction and time,  $t$  respectively.  $A_0$  = absorbance at the beginning of the reaction.

A plot of  $\log k_{\text{obs}}$  versus  $\log [\text{OH}^-]$  was linear with a gradient of 1 (fig. 4) which is an indication that the reaction is first order in  $[\text{OH}^-]$  with an overall second order. Second order rate constants,  $k_2$  were obtained as ratio of  $k_{\text{obs}}$  to  $[\text{OH}^-]$ .

Also constancy of  $k_2$  (Table 1) shows that the reaction is first order with respect to  $[\text{OH}^-]$ . The overall rate of reaction can be represented as:

$$-d[\text{MG}^+]/dt = k_2[\text{MG}^+][\text{OH}^-]$$

Where  $k_2 = 43.36 \pm 0.14 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

Variation of ionic strength,  $I$  of the reaction medium in the range of 0.1-1.0  $\text{mol dm}^{-3}$  was found to decrease the reaction rate (Table 2). This negative salt effect is an indication that the activated complex is formed from oppositely charged ions [10]. A plot  $\log k_2$  versus  $\sqrt{I}$  was linear (fig. 5) with a slope of -1.077 suggesting that the charge on the activated complex is 1.

The effect of dielectric constant,  $D$  of reaction medium on the reaction rate was investigated as described elsewhere [7]. Increasing  $D$  implies increasing polarity of reaction medium. The results on Table 3 show that the rate of reaction decreased with increase in  $D$ , suggesting that there is increase in charge separation. This observation also reinforced the results obtained by varying ionic strength of reaction medium on reaction rate.

The independence of [anions] on reaction rate was studied by making use of  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  Tables 4, 5 and 6 show that there is a decrease in reaction rate. This observation can be explained on the basis of repulsion between  $\text{MG}^+$  and  $\text{OH}^-$  at the rate determining step. Result of this nature is in conformity with reaction proceeding by outersphere mechanistic pathway.

Absence of free radical as possible reaction intermediates was confirmed by the absence of gel or suspension formation that might have resulted from polymerization when acrylamide was added to the partially reacted mixture [8]. Also scanning of the reaction mixture did not show any shift in  $\lambda_{\text{max}}$  (620nm) pointing to the absence of intermediate complex of significant stability.

Based on the above results, the proposed mechanism for this reaction is presented below.

We approach the issue of mechanistic assignment as follows:

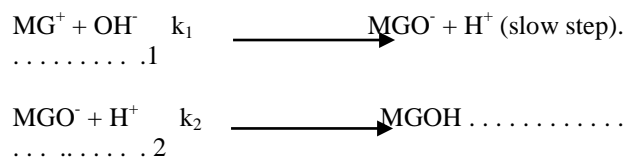
- a) The absence of spectroscopic evidence of binuclear complex formation prior to formation

of activated complex is unlikely and that the activated complex is of outersphere type [5].

- b) The above view is supported by the absence of kinetic evidence in favour of precursor complex formation. Michaelis – Menten plot [9]  $\log 1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  was linear without intercept, suggesting that formation of intermediate is insignificant in this reaction.

- c) Addition of anions ( $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) inhibited the rate of reaction. This is likely due to the interaction between these ions and  $\text{OH}^-$  at the transition state.

The above evidence is in support of outersphere mechanism and is hereby proposed for the reaction.



**Table 1: Pseudo first-order rate constants for the reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, I = 0.5 mol.dm<sup>-3</sup>, T = 22 ± 1<sup>o</sup>C and λ<sub>Max</sub> = 620nm**

$10^2[\text{OH}^-]$ , mol.dm <sup>-3</sup>	$K_{\text{obs}}$ , min <sup>-1</sup>	$K_2$ , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
1.0	0.4733	47.33
1.1	0.5205	47.31
1.2	0.5678	47.32
1.3	0.6170	47.46
1.4	0.6621	47.29
1.5	0.7120	47.44
1.6	0.7600	47.50
1.8	0.8500	47.22

**Table 2: Effect of ionic strength on the rate of reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, [OH<sup>-</sup>] = 1.8 x 10<sup>-2</sup> mol.dm<sup>-3</sup>, T = 22 ± 1<sup>o</sup>C and λ<sub>Max</sub> = 620nm**

$I$ , mol.dm <sup>-3</sup>	$K_{\text{obs}}$ , min <sup>-1</sup>	$K_2$ , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
0.1	2.1971	122.06
0.2	1.5980	88.78
0.3	1.2200	67.78
0.4	0.9921	55.15
0.5	0.8500	47.18
0.6	0.7323	40.68
0.8	0.5231	29.06
1.0	0.3951	21.93



**Table 3: Effect of dielectric constant of reaction medium on the rate of reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, [OH<sup>-</sup>] = 1.8 x 10<sup>-2</sup> mol.dm<sup>-3</sup>, I = 0.5 mol.dm<sup>-3</sup> and T = 22 ± 1<sup>0</sup>C**

Dielectric constant(D)	K <sub>obs</sub> , min <sup>-1</sup>	K <sub>2</sub> , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
81.0	0.856	47.6
80.4	0.840	50.0
79.8	0.811	52.8
79.2	0.794	55.5
78.6	0.760	58.0
77.4	0.707	63.7
76.2	0.653	69.0
75.0	0.586	75.0

**Table 6: Effect of SO<sub>3</sub><sup>-</sup> on the rate of reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, [OH<sup>-</sup>] = 1.8 x 10<sup>-2</sup> mol.dm<sup>-3</sup>, I = 0.5 mol.dm<sup>-3</sup> and T = 22 ± 1<sup>0</sup>C**

10 <sup>3</sup> [NO <sub>3</sub> <sup>-</sup> ], mol.dm <sup>-3</sup>	K <sub>obs</sub> , min <sup>-1</sup>	K <sub>2</sub> , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
0	0.8604	47.8
1	0.7984	44.4
10	0.7861	43.7
20	0.7549	42.0
40	0.7220	40.1
70	0.6595	36.6
100	0.5922	32.9
140	0.5182	28.8
200	0.3932	21.9

**Table 4: Effect of CH<sub>3</sub>COO<sup>-</sup> on the rate of reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, [OH<sup>-</sup>] = 1.8 x 10<sup>-2</sup> mol.dm<sup>-3</sup>, I = 0.5 mol.dm<sup>-3</sup> and T = 22 ± 1<sup>0</sup>C**

10 <sup>3</sup> [CH <sub>3</sub> COO <sup>-</sup> ], mol.dm <sup>-3</sup>	K <sub>obs</sub> , min <sup>-1</sup>	K <sub>2</sub> , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
0	0.8604	47.8
1	0.7722	42.9
10	0.7600	42.2
20	0.7380	41.0
40	0.6910	38.4
70	0.6349	35.3
100	0.5636	31.3
140	0.4769	26.5
200	0.3450	19.2

**Table 5: Effect of NO<sub>3</sub><sup>-</sup> on the rate of reaction of MG and OH<sup>-</sup> at [MG] = 1 x 10<sup>-5</sup> mol.dm<sup>-3</sup>, [OH<sup>-</sup>] = 1.8 x 10<sup>-2</sup> mol.dm<sup>-3</sup>, I = 0.5 mol.dm<sup>-3</sup> and T = 22 ± 1<sup>0</sup>C**

10 <sup>3</sup> [NO <sub>3</sub> <sup>-</sup> ], mol.dm <sup>-3</sup>	K <sub>obs</sub> , min <sup>-1</sup>	K <sub>2</sub> , dm <sup>3</sup> .mol <sup>-1</sup> .min <sup>-1</sup>
0	0.8604	47.8
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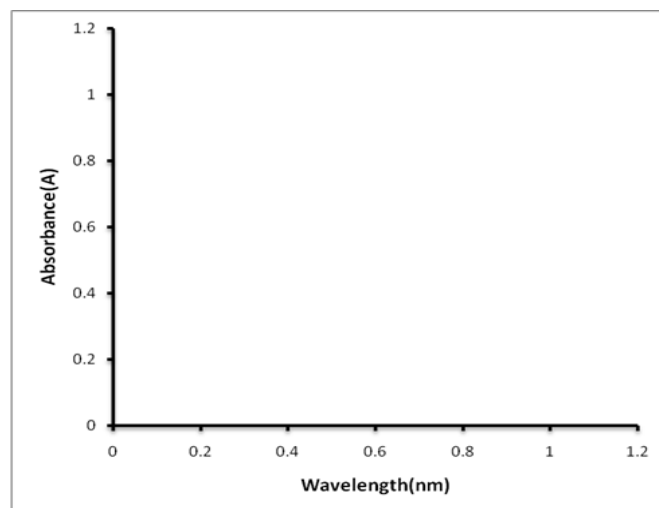


Fig. 1: Spectrum of MG

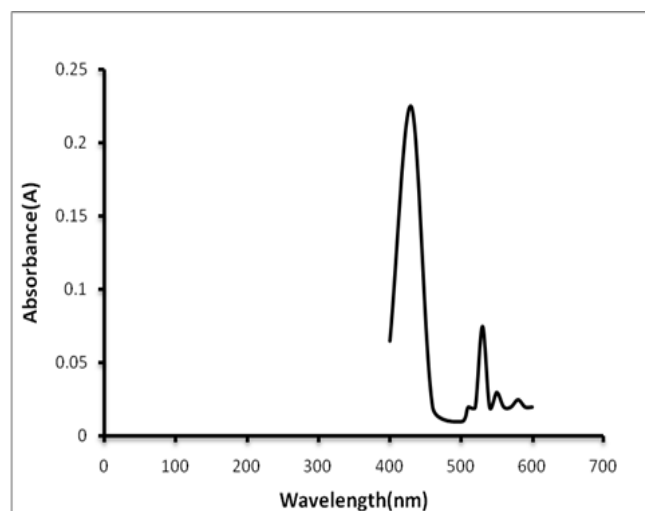
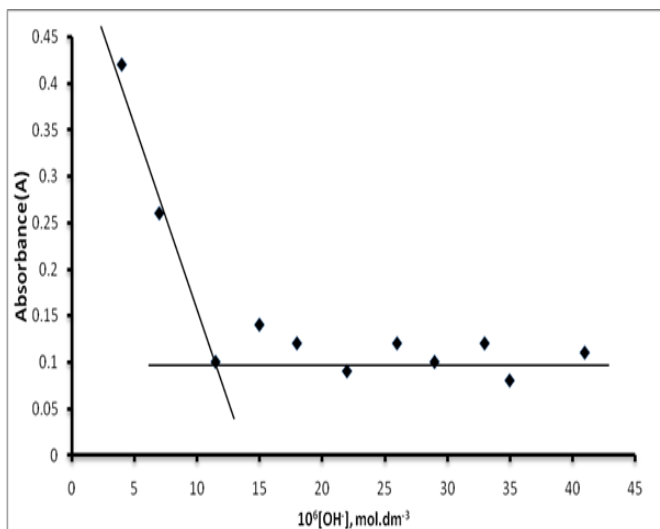
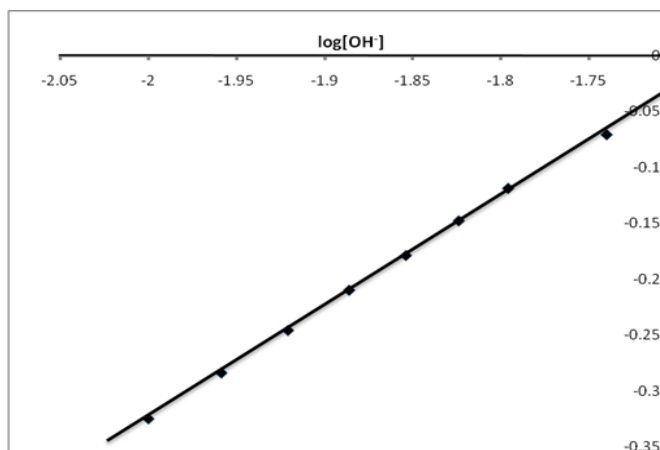


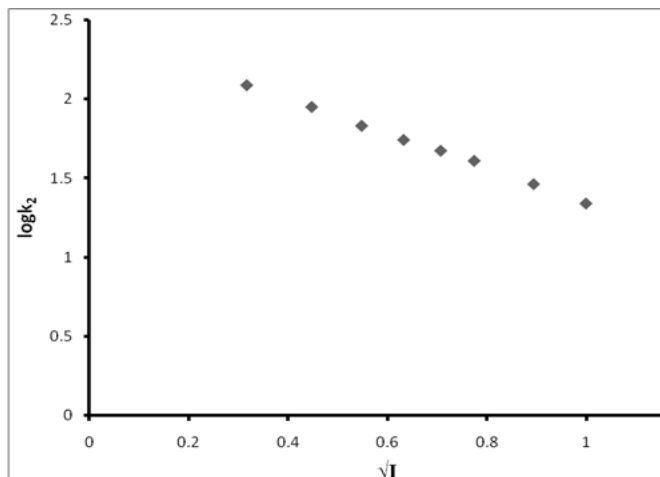
Fig. 2: Spectrum during the reaction of MG and OH



**Fig. 3:** Plot of Absorbance (A) versus  $[\text{OH}^-]$  for the determination of stoichiometry of MG and  $\text{OH}^-$



**Fig. 4:** Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{OH}^-]$  for the determination of the order of MG and  $\text{OH}^-$  reaction



**Fig. 5:** Effect of ionic strength of reaction medium on the rate of MG and  $\text{OH}^-$  reaction

## REFERENCES

- [1] Finar, I.L (1973). Organic Chemistry. Vol.1. The Fundamental Principles. 6<sup>th</sup> ed. The English Language Book Society and Longman Group Ltd. London, 878-887
- [2] Culp, S.G and Beland, F.A (1996). Malachite green: A toxicological review. *J. Am. Coll. Toxicol.* 15, 219
- [3] Alderman, D.J (1985). Malachite green: A review *J. Fish. Dis.* 8(3), 295
- [4] Alderman, D.J and Clifton-Hadley, R.S (1993). Malachite green: A pharmacokinetics study in rainbow trout. *J. Fish. Dis.* 16, 307
- [5] Ukoha, P.O., Agunwa, U.B and Okonkwo, E.M (2001). Kinetics of the oxidation of 4,4'-(phenylmethylene)bis(N,N-dimethylbenzeneamine)(leucomalachite green) by Cr(vi) in aqueous acid media. *J. Chem. Soc. Nigeria* 26(1): 81-86 and all the references therein
- [6] Lawton, J.R (1989). An investigation of fixation and staining of lipids by a combination of malachite green or other triphenylmethane dyes with glutaraldehyde. *J. Microsc.* 154: 83-92
- [7] Idris, S.O, Iyun, J.F and Agbaji, E.B (2009) kinetics of the reduction of tetrakis (2,2'-bipyridine)- $\mu$ -oxodiiron (iii) ion by 1,3-benzenediol in aqueous acid medium. *Transition met. Chem.* 34(2): 205-208
- [8] Mohammed, Y, Iyun, J.F and Idris, S.O (2008). Redox kinetics to the mechanism of the redox reaction of malachite green and permanganate ion in aqueous acid medium. *Afr. J. Pure Appl. Chem.* 3(12): 269-274
- [9] Mohammed, Y, Iyun, J.F and Idris, S.O (2010). Studies into the kinetics and mechanism of the redox reaction of malachite green and nitrite ion in aqueous acid medium. *J. Chem. Soc. Nigeria* 35(1): in the press
- [10] Atkins, P. and de Paula J. (2002). Physical Chemistry, 7<sup>th</sup> ed. Oxford University Press. P. 962