

KINETICS AND THERMODYNAMIC STUDY OF ALKALINE FADING OF MALACHITE GREEN IN AQUEOUS SOLUTION

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Abstract: Kinetic and thermodynamic study of alkaline fading of malachite green in aqueous solution via pseudo-first order kinetics at 618nm is reported using UV-1800 Shimadzu Spectrophotometer. The reaction revealed first order dependence with respect to malachite green concentration and first order dependence to hydroxyl ion concentration. Michaelis-Menten plot showed the presence of an intermediate complex and the reaction is dependent on ionic strength of the solution. Activation energy (E_a) and activation parameters like ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were obtained from Arrhenius plot and Eyring's equation. A mechanism is postulated based on the kinetic and spectroscopic studies.

Keywords: malachite green(MG); sodium hydroxide; potassium nitrate; kinetics; activation parameters

1. Introduction:

Malachite green is a cationic triphenylmethane dye and has several diverse uses. It has found great use as an antibacterial and antifungal agent, as a dye for anionic substrates like silk, leather, cotton and paper, as an intestinal anthelmintic and as a wound disinfectant¹. Therefore, because of its industrial importance, it constitutes one of the dyes released into the environment as industrial effluents which are carcinogenic and toxic to aquatic life². Malachite green has adverse effects on human immune system and reproductive system³. Owing to this hazardous effect, extensive researches have been reported on the sorption chemistry and toxicological effect of the dye⁴⁻⁸. Scanty research works on the chemistry of malachite green includes, the effect of surfactants on its hydrolytic reaction have also been investigated^{9,10,11}, oxidation of malachite green¹². It is worthy to state that unlike adsorption, photolysis and several other techniques which are slow and expensive for the removal of malachite green from industrial effluents, hydrolytic process involves chemical decomposition of the dye which is the most effective way of removal. However, the chemistry of its hydrolysis has not received much attention. Hence this informed the reason for this research with the view to determining a mechanistic pathway for the reaction.

2. Experiment:

2.1. Material:

All chemicals and reagents used were of analar grade and stock solutions were prepared with double distilled water.

2.2 Methods:

2.2.1. Stiochiometry:

The absorbances at infinite time of solutions containing [NaOH] in the range 6.67×10^{-4} - 4.00×10^{-3} M and constant [MG]₀ and Ionic strength, $\mu = 0.05$ M were monitored. The stoichiometry of the reaction was determined spectrophotometrically from the plot of Absorbance versus [NaOH] curve.

2.2.2. Kinetic measurement:

The reaction was investigated via pseudo-first order conditions. Appropriate quantities in the order; Malachite green, potassium nitrate and sodium hydroxide were measured from the stock solutions (kept in a water bath for 30 minutes) into a quartz cuvette. Consequently, decrease in absorbance of Malachite green with time was monitored at 618nm with a Shimadzu UV-1800 double beam UV-Vis Spectrophotometer equipped with a thermostated cell thermostat for 50 minutes. The observed first order rate constants(k_{obs}) were determined from the slope of $\ln A$ versus time.

$$MG^+ + OH^- \xrightarrow{k_2} P$$

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

$$\frac{-d[MG^+]}{dt} = k_1[MG^+]$$

where,

$$k_1 = \text{pseudo first order rate constant}(s^{-1})$$

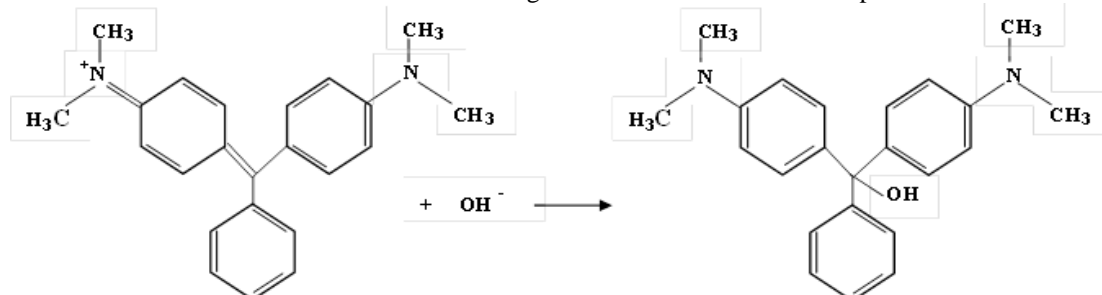
$$k_2 = \text{second order rate constant}(M^{-1}s^{-1})$$

$$k_1 = k_2[OH^-]$$

$$k_2 = \frac{k_1}{[OH^-]}$$

3. Results and discussion:

Stoichiometric studies revealed one mole Malachite green to one mole OH^- consumption.



The observed rate constant (k_{obs}) increased with increase in $[MG]$ as shown in Table 1. The dependence on $[MG]$ is first order from the slope (unity) of the plot of $\ln k_{obs}$ versus $\ln [MG]$. The hydrolytic reaction increased with increase in $[NaOH]$ as shown in Table 2. The slope of a plot of $\ln k_{obs}$ versus $\ln [NaOH]$ was also unity, implying a first order dependence with respect to $[NaOH]$ and the second order rate constant obtained from the plot of k_{obs} versus $[NaOH]$ was $1.08 M^{-1}s^{-1}$. It is noteworthy that the presence of an intermediate complex was observed as the plot of $1/k_{obs}$ versus $1/[NaOH]$ gave an intercept¹³(Fig.1).

 Table 1: Effect of $[MG]$

$10^5 [MG]/M$	$10^3 k_{obs}/s^{-1}$
1.00	0.65
2.00	0.95
3.00	1.58
4.00	1.78
5.00	2.25
6.00	2.60
7.00	2.96

$[NaOH] 1.67 \times 10^{-3} M$ $\mu=0.09M$ $T=298K$

 Table 2: Effect of $[OH^-]$

$10^3 [OH^-]/M$	$10^3 k_{obs}/s^{-1}$
0.67	0.78
1.00	1.21
1.67	1.75
2.00	2.38

2.50	2.82
3.00	3.43
3.50	3.67
4.00	4.11

[MG] $1.00 \times 10^{-5} \text{M}$ $\mu=0.05 \text{M}$ $T=298 \text{K}$

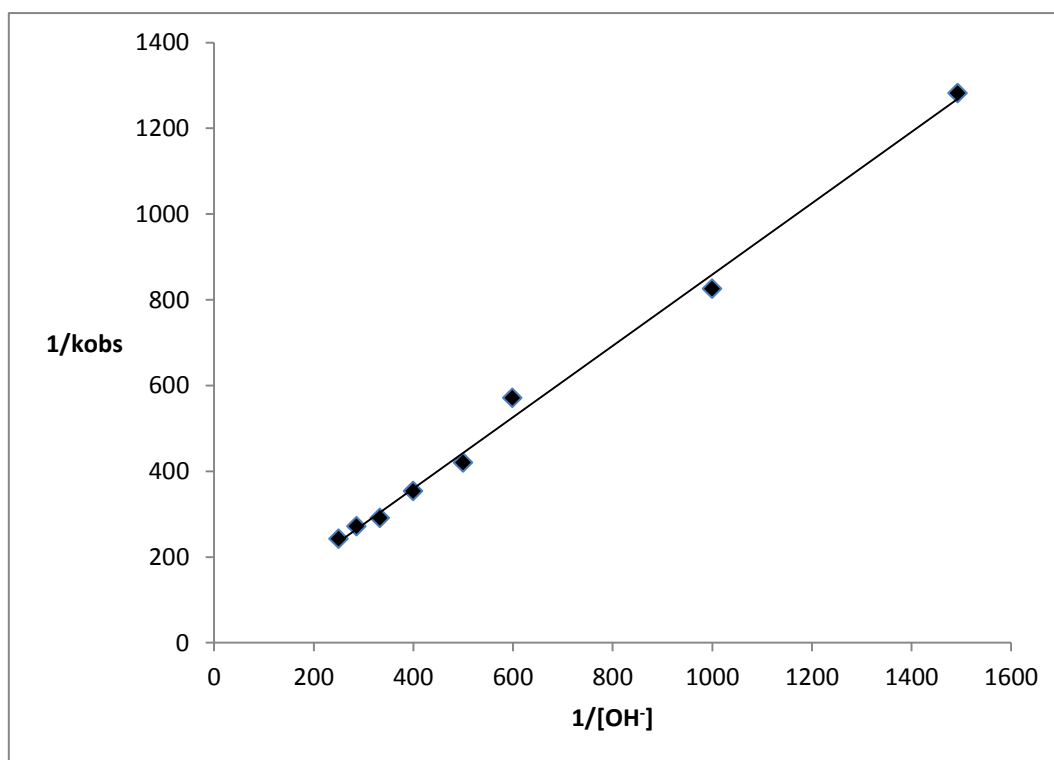


Figure 1: Plot of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$

Furthermore, the observed rate constant decreased with increase in the ionic strength of the solution. The slope of the plot of $\log k_{\text{obs}}$ versus $\sqrt{\mu}$ gave -1, suggesting the presence of -1 and +1 ionic charges on the reactants at the rate determining step¹⁴ (Fig.2). Increase in temperature resulted to an increase in the observed rate constants (k_{obs}). Hence, from the slope of Arrhenius plot of $\ln k_{\text{obs}}$ versus $1/T$ activation energy (E_a) was obtained as 14.50 kJmol^{-1} . The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and Gibb's free energy of activation (ΔG^\ddagger) were obtained from Eyring's equation as $-0.26 \text{ JK}^{-1}\text{mol}^{-1}$, 11.99 kJmol^{-1} and 89.47 kJmol^{-1} respectively.

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{k'}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right)$$

$$\ln\left(\frac{k'}{h}\right) = 23.76$$

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

k = observed rate constant
 T = Temperature
 ΔH^\ddagger = Enthalpy of activation
 ΔS^\ddagger = Entropy of activation
 ΔG^\ddagger = Free Gibb's energy of activation
 R = Molar gas constant
 k' = Boltzmann's constant
 h = Plank's constant

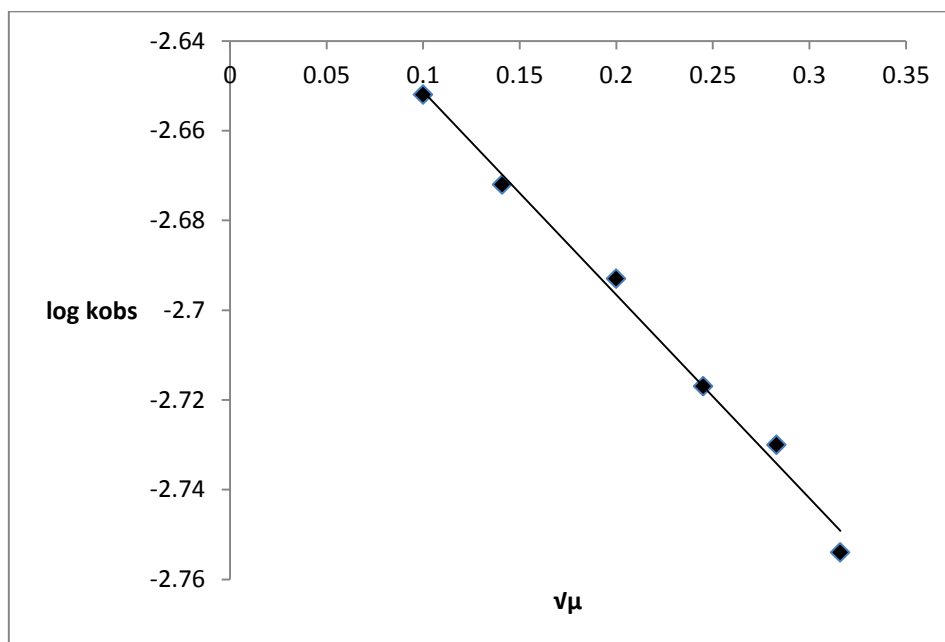


Figure 2: Plot of $\log k_{obs}$ versus $\sqrt{\mu}$ ([MG] $1.00 \times 10^{-5}M$ [NaOH] $1.67 \times 10^{-3}M$ T=298K)

Test for free radicals: Addition of acrylamide solution to the reaction mixture gave no polymerization, implying the absence of free radicals in the reaction¹⁵.

Product Analysis: Sharp absorption at 1474.2 cm^{-1} signals the presence of C=C aromatic ring. Furthermore, peak at $3610\text{-}3640\text{ cm}^{-1}$ is due to the presence of O-H, which suggests carbinol as the major product of the hydrolytic reaction.

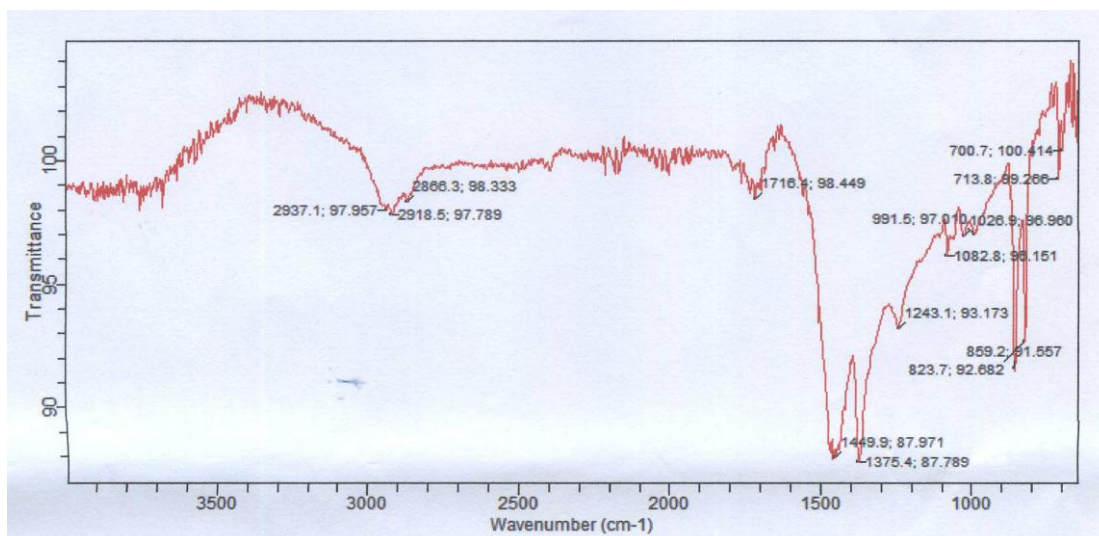
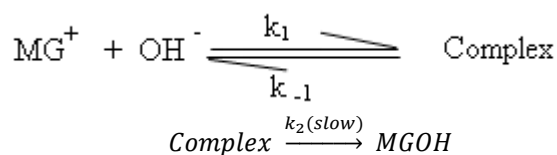


Figure 3: FTIR Spectrum of the product

Therefore, possible mechanism consistent with the above kinetic and spectroscopic results is hereby presented:



$$\text{Rate} = k_2[\text{Complex}] \quad (1)$$

$$\frac{d[\text{Complex}]}{dt} = k_1[\text{MG}^+][\text{OH}^-] - k_{-1}[\text{Complex}] - k_2[\text{Complex}] \quad (2)$$

$$\frac{d[\text{Complex}]}{dt} = k_1[\text{MG}^+][\text{OH}^-] - (k_{-1} + k_2)[\text{Complex}] \quad (3)$$

Applying steady state approximation

$$0 = k_1[\text{MG}^+][\text{OH}^-] - (k_{-1} + k_2)[\text{Complex}] \quad (4)$$

$$k_1[\text{MG}^+][\text{OH}^-] = (k_{-1} + k_2)[\text{Complex}] \quad (5)$$

$$[\text{Complex}] = \frac{k_1[\text{MG}^+][\text{OH}^-]}{k_{-1} + k_2} \quad (6)$$

Substituting equation (6) in (1)

$$\text{Rate} = \frac{k_1 k_2 [\text{MG}^+][\text{OH}^-]}{k_{-1} + k_2}$$

where, $k = \frac{k_1 k_2}{k_{-1} + k_2}$.

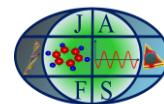
$$\text{Rate} = k[\text{MG}^+][\text{OH}^-]$$

4. Conclusion:

The hydrolytic reaction is first order with respect to malachite green ditto for hydroxyl ion concentrations. Hydrolysis of poisonous triphenyl methane dyes like malachite green is the most effective, least cost effective and fastest way of removing the dye from industrial effluents. The hydroxyl ion attacks the carbon within the planar ring of the malachite green, thereby destroying the conjugation configuration on the dye which leads to the formation of carbinol.

Reference:

- [1] Nelson C.(1974). A Review of the Literature on the Use of Malachite Green in Fisheries. U.S Department of the Interior, Fish and Wildlife Service, Western Fish Disease Laboratory 1-20.
- [2] Cho B, Yang T, Blankenship L.R, Moody J.D, Churchwell M, Bebland F.A, Culp S.C(2003). Synthesis and Characterization of N-dimetylated Metabolites of Malachite green and Leucomalachite green, Chemical Research in Toxicology, 16, 285-294.
- [3] Srivastava S, Sinha R and Roy D(2004). Toxicological effects of Malachite green, Aquatic Toxicology, 66, 319-329.
- [4] Hema M, Arivoli S(2008). Adsorption Kinetics and Thermodynamics of Malachite Green unto Acid Activated Cost Carbon, J. Appl. Sci. Environ. Manage, Vol.12(1), 43-51
- [5] Singh J and Kaur G(2013). Freundlich, Langmuir Adsorption Isotherms and Kinetics for the Removal of Malachite Green from Aqueous Solutions using Agricultural Waste Rice Straw, Int. J. Environ. Sci. Vol. 4, No3, 250-258.
- [6] Deokar R and Sabale A(2014). Biosorption of Methylene Blue and Malachite Green From Binary Solution onto *Ulva lactuca*, Int. J. Curr. Microbiol. App. Sci. 3(5), 295-304.
- [7] Belay K and Abebe M(2014). Removal of Malachite Green from Aqueous Solutions by Adsorption Using Low Cost Biosorbent Neem Leaf (*Azadirachta Indica*), Merit Research Journals, Vol.2(4), 86-92.
- [8] Chen Z, Deng H, Chen C, Yang Y, Xu, H(2014). Biosorption of Malachite Green from Aqueous Solutions by *Pleurotus ostreatus* Using Taguchi Method, J. Environ. Health Sci and Engr, 12:63,1-10.
- [9] Samiey B, Toosi R(2009). Kinetic Study of Malachite Green Fading in the Presence of TX-100, DTAB, SDS, Bull. Korean Chem. Soc. Vol. 30 No 9, 2051-2056
- [10] Soriyan O, Owoyomi O, Ogunniyi A(2008). The Basic Hydrolysis of Malachite green in β -cyclodextrin/cetyltrimethylammonium Bromide(CTAB) Mixed system, Acta Chimica Slovenica, Vol. 55 issue 3, 613-616.
- [11] Dasmandal S, Mandal H. K, Kundu A, Muhapatra A.(2014). Kinetic investigations on Alkaline Fading of Malachite Green in the Presence of Micelles and Reverse Micelles, Journal of molecular liquids, 193, 123-131.
- [12] Mohammed Y, Iyuan J.F and Idris S.O(2009). Kinetic Approach to the Mechanism of the Redox Reaction of Malachite Green and Permanganate Ion in Aqueous Acidic Medium, Afri. J. Pure and Applied Chem., Vol. 3(12), 269-274.
- [13] Kumar P, Panday D, Kothari S(2011). Kinetics and Mechanism of the Oxidation of Aliphatic Aldehydes by Benzimidazolium Dichromate, Croat. Chemica Acta 84(1), 53-61.



[14] Sharma K.K, Sharma L.K(2008). A Textbook of Physical Chemistry, Fourth Revised Edition, UBS Publishers, 564-566.

[15] Saraswat S, Sharma V, Banerji K.K(2003). Kinetics and Mechanism of Aliphatic Alcohols by Quinolinium Bromochromate, Proc.Indian Acad. Sci(Chem.Sci). Vol. 115, No1, 75-82.