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KINETICS OF REACTION BETWEEN MALACHITE GREEN AND HYDROXYL ION IN THE PRESENCE OF REDUCING SUGARS.

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Abstract

The reaction was studied via pseudo first order kinetics using uv-1800 Shimadzu spectrophotometer with a thermostated cell compartment and interfaced with a computer . The reaction showed first order with respect to malachite green and sugar and hydroxyl ion concentrations. However, the reaction was independent of ionic strength and showed no dependence on salt effect, indicating an inner sphere mechanism for the reaction. There was no polymerization of the reaction mixture with acrylonitrile, indicating absence of radicals in the course of the reaction. Michaelis-Menten plot indicated the presence of a reaction intermediate in the rate determining step. The activation parameters of the reaction have been calculated and products were elucidated by FTIR spectroscopy. The stoichiometry of the reaction is 1:1. A mechanism consistent with the above facts has been suggested.

Keywords: Malachite green(MG), sodium hydroxide, Glucose, Fructose, Xylose.

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Introduction

Malachite green is a triphenylmethane dye which has wide range of industrial applications, most especially in aquaculture production because of its antibacterial, antifungal and antiparasitic properties(1) . However, they are toxic to human as they have been confirmed to be mutagenic and carcinogenic (2). Owing to its hazardous effect, several researches have been reported on the best ways to remove it in water or industrial effluents mainly by biosorption(3,4,5,6). It has been established that wood fibre of phoenix tree(*Firmiana Sinplex*) is an effective adsorbent for malachite green(7).

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Fading of malachite green(MG) in the presence of hydroxyl ion has been attributed to the hydroxide ion attack on the central C atom of the planar ring system of malachite green, thereby destroying its conjugation orientation.It has been found that sugars such as dextrose, lactose and sucrose increases the rate of fading of dyes in general (8). Hitterto, there has been no report on the kinetics and mechanism of alkaline malachite green fading in sugars. However, few or scanty investigations have been reported on the kinetics of alkaline malachite green fading in alcohols and in the presence of surfactants(9,10).

Hence the need to study the effect of some reducing sugars on the alkaline fading of malachite green with the view to determining the mechanism via a vis the mechanism earlier proposed for the oxidation of sugars in sodium hydroxide medium(11).

Materials and methods

Analar grade malachite green, NaOH, KOH, glucose, fructose and xylose were used and the solutions were prepared in doubly distilled water.

The reaction products were characterized by FTIR and the reaction showed no presence of radicals as there were no polymerization on addition of acrylonitrile to the reaction mixture.

Spectral Measurement

λmax of dilute solution of malachite green was obtained at 617 nm using a uv-1800 Shimadzu spectrophotometer.

Kinetic Measurements

The reactions were performed under pseudo-first order conditions by maintaining a large excess (x10 or greater) of sugar over malachite green. The kinetic data were obtained by monitoring change in absorbance of malachite green at absorption maximum as a function of time with a UV- 1800 Shimadzu spectrophotometer connected to a thermostated cell compartment and interfaced with a computer. Appropriate quantities of the solution of sugar, potassium nitrate, sodium hydroxide and malachite green were measured into the cuvette. Consequently, the reaction was kick started after adding requisite volume of the malachite green solution (All stock solutions were kept in the water bath for 30 minutes before the kinetic runs). The kinetic data were obtained via pseudo- first order condition with the concentration of the sugar in large excess compared with the oxidant concentration. The pseudo- first order rate constant (k_{obs}) were calculated.

Results and Discussion

Stoichiometry and product analysis

The stoichiometry of the reaction was determined by spectroscopic titration. Absorbances of solutions containing various concentrations of sugar within the range 1.00 x 10^{-2} to 6.00 x 10^{-2} and a constant $[MG]_o$ of 1.00 x 10^{-3} and constant $[NaOH]_o$ of 6.00 x 10^{-2} and $[KNO_3]_o$ of 0.25M were measured at 710nm after the reaction had gone to completion. The stoichiometry was evaluated from the plot of absorbance vs [sugar] curve and was found to be 1:1.

Effect of [MG] on the observed rate constant

A plot of In k_{obs} vs In[MG] gave a slope equal to 1, indicating a first order dependence. The reaction showed an increase in rate constant with increase in [MG] as shown in fig.1.

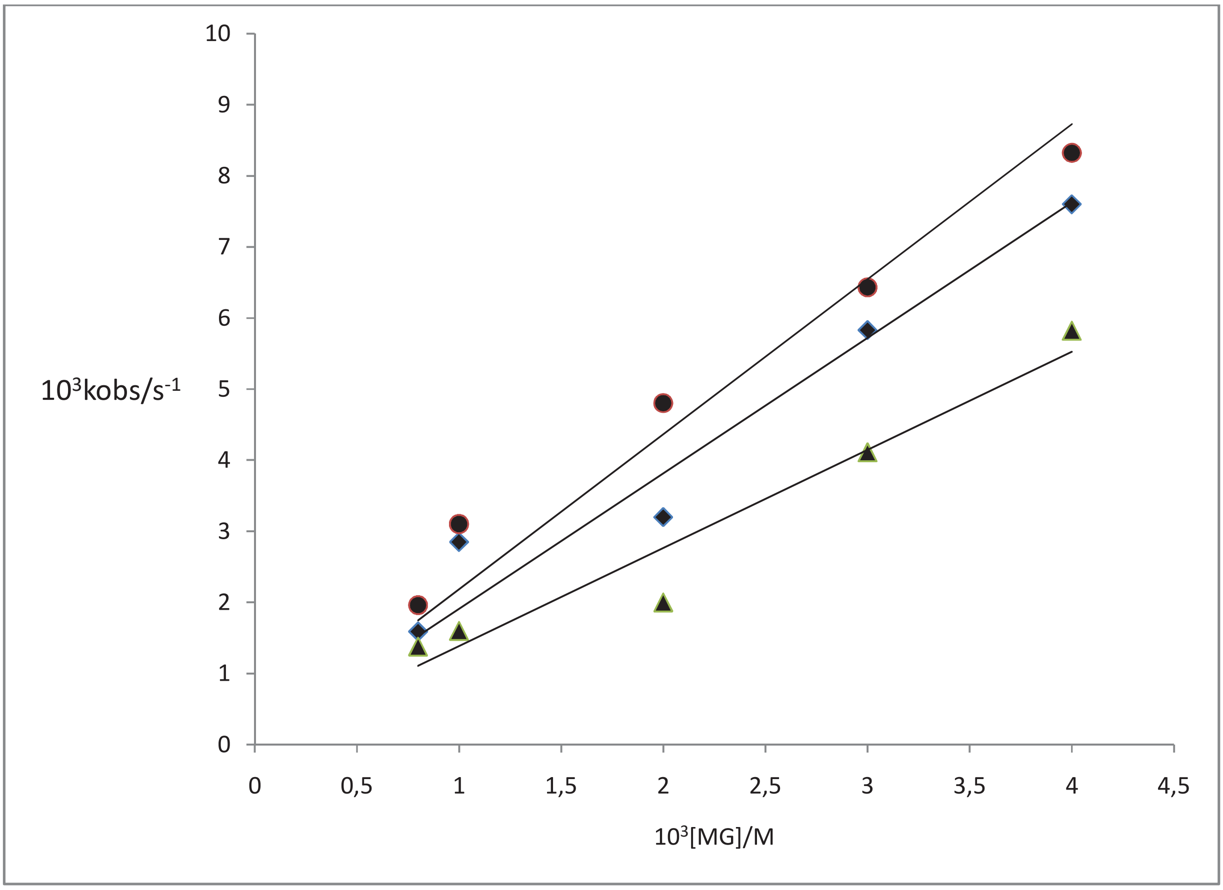


Fig. 1: Plot of k_{obs} vs [MG]

(● Fructose ■ Glucose ▲ Xylose)

Effect of [sugar] on the observed rate constant

As the concentration of sugars increases, there is increase in the rate constants as shown in table 1. The plot of In k_{obs} vs In[sugar] shows that the reaction increases with increase in sugar concentrations, indicating that the complex formation took place between sugar and malachite green and the slope of this plot is unity, implying a first order dependence on [sugar]. The plot of $1/k_{obs}$ vs 1/[s] gave an intercept , revealing the presence of an intermediate complex as shown in fig.2. Second order rate constants are 0.152 $M^{-1}S^{-1}$(Glucose), 0.138 $M^{-1}S^{-1}$ (Fructose), 0.125 $M^{-1}S^{-1}$ (Xylose).

Table 1: Effect of [sugar] on reaction rate

10^2[S]/M	$10^3k_{obs}/s^{-1}$		
	Glucose	Fructose	Xylose
1.00	1.81	2.10	1.73
2.00	3.60	3.40	2.81
3.00	5.12	4.75	3.62
4.00	6.84	6.02	4.80
6.00	8.10	7.41	6.51

[MG] 1.00 x 10^{-3}M [OH^-] 6.00 X 10^{-2}M I= 0.25M T=298K

Effect of [OH^-] on the observed rate constant

Increase in [OH^-] resulted into increased reaction rate as shown in table 2 . The slope of a plot of Ink_{obs} vs In[OH^-] also showed first order dependence.

Table 2: Effect of [OH-] on reaction rate

10^2[OH^-]/M	$10^3k_{obs}/s^{-1}$		
	Glucose	Fructose	Xylose
1.00	1.98	1.81	2.20
2.00	3.14	2.30	3.00
3.00	4.22	3.82	4.21
4.00	5.05	4.85	5.30
5.00	6.70	6.25	6.00
6.00	8.10	7.41	6.91

[MG] 1.00 X 10^{-3}M [S] 2.00 X 10^{-2}M I= 0.25M T= 298K

Effect of ionic strength on the observed rate constant

The reaction rate was independent of the ionic strength of the solution. A plot of Ink_{obs} vs $I^{1/2}$ gave a straight line with slope equal to zero as shown in fig.3, which implies the presence of a neutral molecule in the rate determining step.

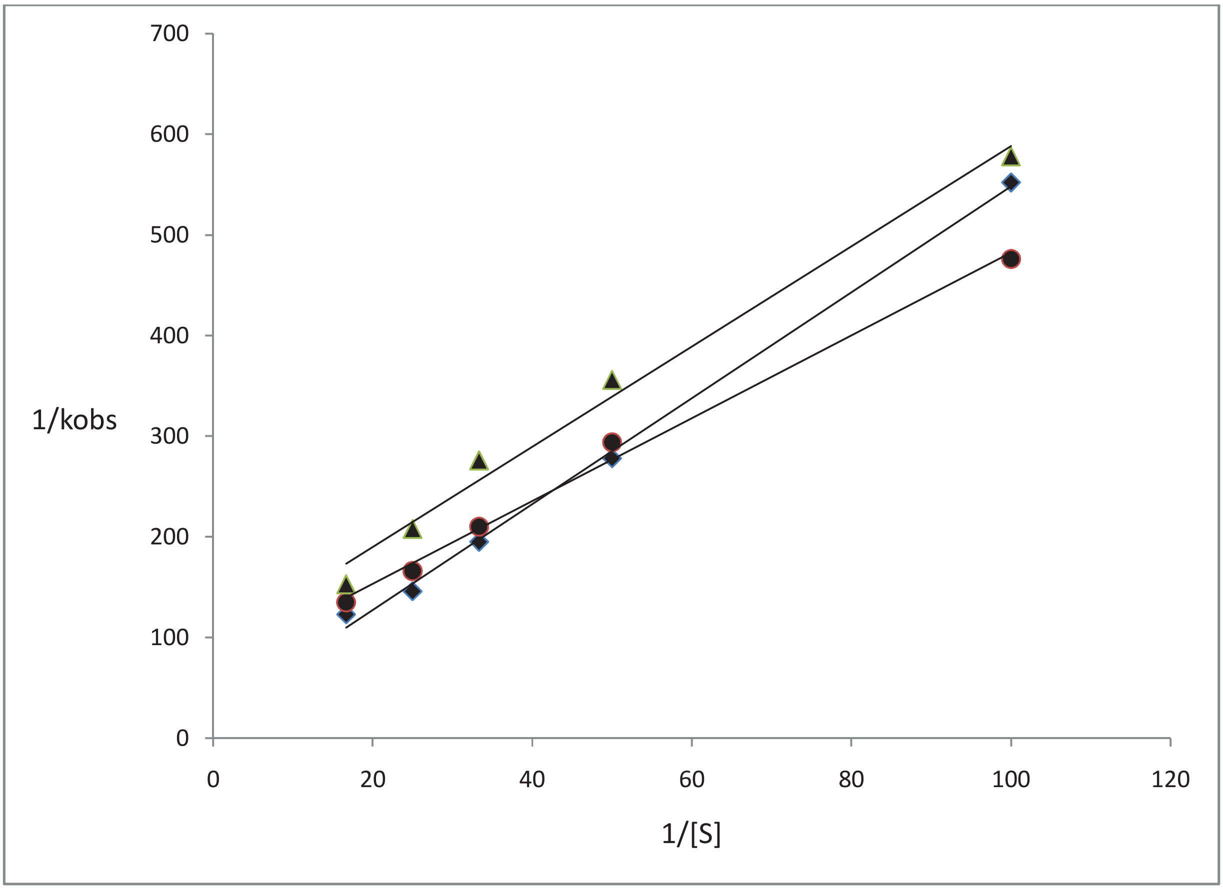


Fig.2: Plot of $1/k_{obs}$ vs 1/[S]

(● Fructose ■ Glucose ▲ Xylose)

Salt effect on the observed rate constant

The addition of KCl and $NaNO_3$ salts did not affect the reaction rate as shown in fig.4. This reveals an inner sphere mechanism for the reaction.

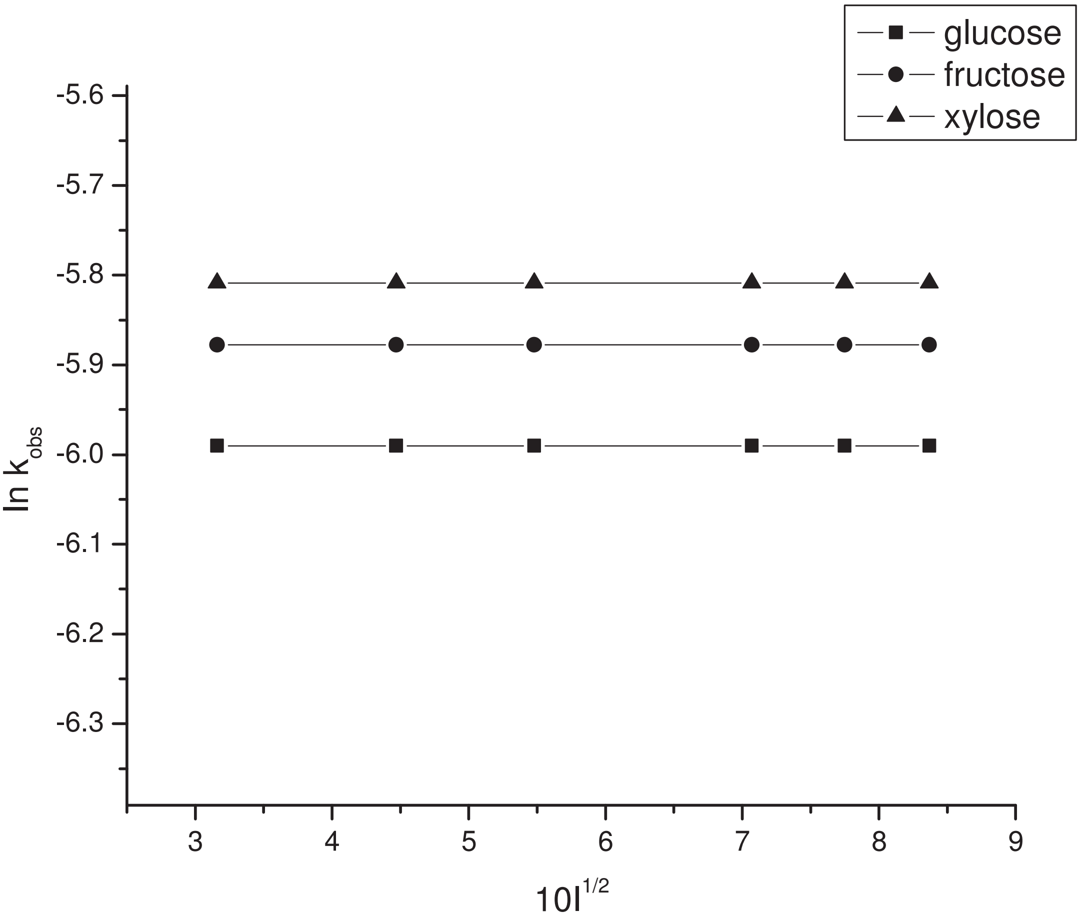


Fig. 3: Plot of $\ln k_{obs}$ vs $I^{1/2}$

Effect of temperature and determination of activated parameters

The effect of temperature on the observed rate constants were determined by varying the temperature within 298K- 308K and concentrations of all the reactants were constant: [MG] 1.00 X 10^{-3}, [sugar] 2.00 x 10^{-2}M, [OH^-] 6.00 x 10^{-2}M and I= 0.25M. The observed rates constants at different temperatures were determined and the values of activation parameters were calculated using the below relationship and shown in table 3. The result showed that the rate of reaction increases with increase in temperature as this is evident by the high negative values of entropies of activation. Moreover, nearly constant values of Gibbs' free energies of activation suggests a similar mechanism for all the sugars.

Table 3: Activation parameters

Sugar	Ea(kJmol^{-1})	ΔH$^{\#}$(kJmol^{-1})	ΔS$^{\#}$(kJK^{-1}mol^{-1})	ΔG$^{\#}$(kJmol^{-1})
Glucose	23.52	21.04	-0.182	75.28
Fructose	25.12	22.64	-0.177	75.38
Xylose	31.34	28.86	-0.156	75.35

[MG] 1.00 x 10^{-3}M [sugar] 2.00 10^{-2}M [OH^{-}] 6.00 X 10^{-2}M I= 0.25M T=298K

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

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \ln\left(\frac{k^{/}}{h}\right) + \left(\frac{\Delta S^{\#}}{R}\right)$$

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

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

k = Rate constant

T= Temperature

ΔH$^{\#}$= Enthalpy of activation

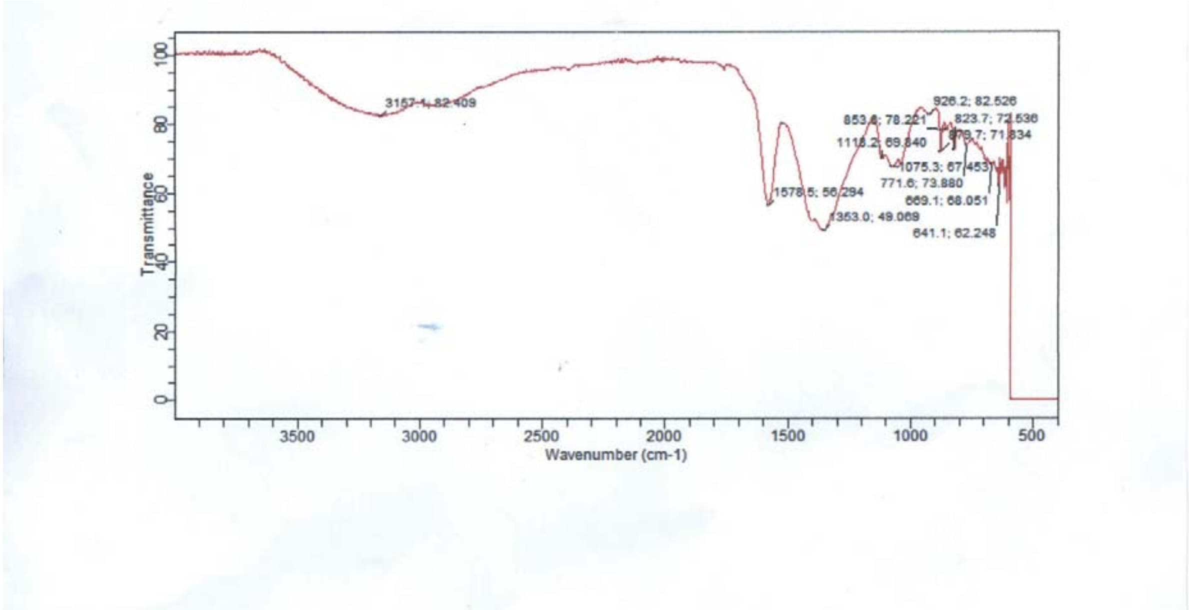
ΔS$^{\#}$= Entropy of activation

ΔG$^{\#}$ = Free Gibb's energy of activation

R= Molar gas constant

k$^{/}$= Boltzmann's constant

h= Plank's constant



FTIR Spectrum of the product.

Mechanism and Rate Law:

The non-dependence of the oxidation reaction on ionic strength indicates the presence of a neutral molecule in the rate determining step. Same values of $\Delta G^{\#}$ indicates same mechanism for the reaction and negative values of $\Delta S^{\#}$ revealed entropy decrease upon achieving the transition state, which often indicate an associative mechanism and it shows that the reaction occurred between ions of similar charges. The FTIR spectrum of the product showed very broad –OH stretching at 3400-2400 cm^{-1}, C=O stretching at 1730-1700 cm^{-1} and C-O stretching between 1320-1210 cm^{-1}which can be attributed to the presence of carboxylic acid. Michaelis-Menten plot showed the presence of an intermediate complex. Relatively low values of $\Delta H^{\#}$ revealed the absence of high energy free radicals.

Considering the above results, the following reaction mechanism is hereby proposed. The alkaline fading of malachite green in the presence of sugars proceeds via the conversion of sugars to their corresponding enediols which of course is a fast step. Then the enediol reacts with malachite green via an outer sphere mechanism to give a complex (slow step) which in turn decomposes into products.

$$S + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} enediol(E)$$

$$E + MG \xrightarrow{k_2(slow)} products$$

$$\frac{-d[MG]}{dt} = k_2[E][MG] \qquad (1)$$

$$\frac{d[E]}{dt} = k_1[S][OH^-] - k_{-1}[E] - k_2[E][MG] \qquad (2)$$

$$0 = k_1[S][OH^-] - k_{-1}[E] - k_2[E][MG]$$

$$k_1[S][OH^-] = k_{-1}[E] + k_2[E][MG]$$

$$[E] = \frac{k_1[S][OH^-]}{k_{-1} + k_2[MG]} \qquad (3)$$

$$From\ equations\ (1)\ and\ (3)$$

$$\frac{-d[MG]}{dt} = \frac{k_2 k_1[S][OH^-][MG]}{k_{-1} + k_2[MG]} \qquad (4)$$

$$Limiting\ condition$$

$$If\ k_{-1}\ is\ far\ greater\ than\ k_2[MG].\ Then\ eq.\ 4\ becomes$$

$$\frac{-d[MG]}{dt} = K_1 k_2[S][OH^-][MG]$$

Conclusion

The research work showed that the mechanism of alkaline malachite green fading in reducing sugar is similar to that of the oxidation of sugars in alkaline medium. The reaction product as shown by the FTIR spectrum revealed the presence of carboxylic acid. This implies that sugars are been oxidized to their corresponding acids by malachite green and malachite green was decolorized via reduction process. However, in the absence of sugar, hydroxyl ion decolorizes malachite green by attacking the central C atom of the planar ring system of malachite green, thereby destroying its conjugation orientation which could have resulted in the production of carbinol.

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