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Aerobic Oxidation of D-Glucose by Methylene Green in Alkaline Aqueous Solution by Visible Spectrophotometry

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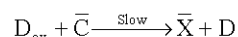
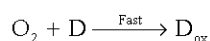
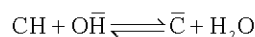
Abstract: Color fading was observed during the Methylene Green (MG) catalyzed oxidation of D-glucose (RH) in alkaline aqueous solution. The kinetics of aerobic oxidation of D-glucose with MG⁺ was investigated by change in optical density of the dye using spectrophotometer. The reaction was first order with respect to the concentration of substrate. The oxidation proceeds via complex formation between glucose and methylene green and the rate constant of the decay of the complex was determined. The oxidation-reduction reactions were observed at various experimental parameters like concentration of methylene green as well as glucose, ionic strength of the medium and temperature. Rate of reaction was found to be dependent upon concentration of glucose as a reducing agent and independent upon the concentration of dye. An increase in the temperature results in elevation of rate of reaction. Activation parameters such as E_a, ΔH*, ΔG* and ΔS* were determined by investigating rate of reaction at different temperature with different ionic strength. A mechanism consistent with above investigations has been proposed.

Key words: Catalyzed oxidation, complex, decay

INTRODUCTION

The kinetics of aerobic oxidation of D-glucose by methylene blue followed first order reaction (Adamcikova *et al.*, 1999). The rate constant was increased with the increase in concentration of glucose. The color change results from the reversible oxidation-reduction reaction of the methylene blue indicator. In alkaline solution, glucose is oxidized to D-gluconic acid or alpha glucolactones. Spatial patterns formation in methylene blue catalyzed oxidation of fructose at alkaline pH was reported by Adamcikova *et al.* (2000). He also reported that long-lasting structure were formed in gel system.

The blue bottle (Cook *et al.*, 1994) experiment shows that mixture of glucose and methylene blue turn color less when allowed to stand but on shaking, dissolved oxygen gives blue color of the dye according to the following simple reaction mechanism



Where D is reduced dye

X = oxidation product

The kinetic (De Lucca *et al.*, 2002; Jonnalagadda and Gellapalli, 2000; Kamat and Lichtin, 1982) of the hydride transfer reaction between leuco methylene blue and thionine was investigated spectrophotometrically by means of stopped flow technique (De Lucca *et al.*, 2002). LMB (leuco methylene blue) and LTH (leuco thionine) were produced by photo reduction of methylene blue and thionine with triethyl amine in ethanol. The photoreduction of thionine, methylene blue and methylene green with different reducing agents like thiourea, methylamine, ethylamine, trimethyl amine and triethyl amine were determined in relation with quantum yield of reaction mixture (Liu *et al.*, 2000; Mowry and Paul, 1999; Quitevis *et al.*, 2000; Uddin *et al.*, 2001; Uddin and Hasnain, 2002). Photoreduction were found to be depending upon the concentration of reductants while independent upon the concentration of dye (Uddin, 2000; Snehalatha *et al.*, 1997).

The aim of present investigation was to study the oxidation of monosaccharide via reduction of the methylene green, as the reduction of this dye with respect to carbohydrate has not been studied yet. This study will examine the kinetics of oxidation of glucose with methylene green in alkaline medium by spectrophotometrically. The reaction will follow the change in absorbance due to formation of leuco dye in presence of glucose in alkaline medium. Results will be discussed in relation with the effect of concentration of glucose, methylene green and NaOH, temperature and ionic strength of the medium. The oxidation proceeds via complex formation between aldose concentration and methylene green and the rate constant of the decay of the complex will be determined. A mechanism will be proposed based on above findings.

MATERIALS AND METHODS

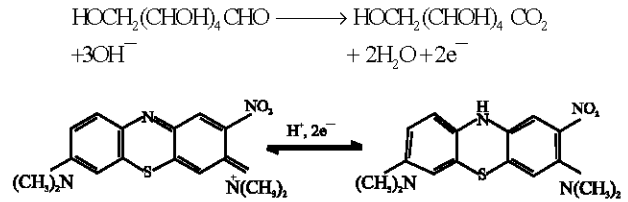
All reagents like methylene green, D-glucose and sodium hydroxide were purchased from E. Merck. These compounds were used as received. All solutions were prepared in conductivity water. A high precision stop watch was used to monitor the change in absorbance with respect to time.

Kinetics measurements: Three sets of mixtures were prepared from stock solutions. In each set one species was varied while other two were kept at fixed initial concentration. In all sets the concentration of MG⁺ was less than 1% of the alkali and glucose. The three contents were mixed together and portion was transferred to the cuvette (1.00 cm) to record a change in optical density of methylene green.

Kinetic measurements were made with visible spectrophotometer at λ_{m ax} 660 nm of methylene green. Kinetics runs were made at time intervals of 200 to 400 s depending on the specific reaction rates. Ordinary light levels had no observable effects on rate of reaction

RESULTS AND DISCUSSION

Kinetics investigation shows that the MG⁺ concentration obeys the Beer-Lambert law A = εcl, Fig. 1 represents the absorption spectra of MG⁺ in aqueous medium at maximum wavelength 660 nm. Table 1 showed that reaction is first order with respect to glucose, methylene green and sodium hydroxide. Oxidation proceeds via reduction of the dye (MGH) by abstraction of one proton from RH (glucose) with transfer of two electrons. This results in the formation of gluconic acid as oxidation product of glucose in presence of air by following reaction.



The oxidation process was investigated under aerobic condition. It was found that reaction between MG⁺ and RH is very fast and proceeds almost to completion and back reaction was not observed. The slope of a plot of the log of the different consecutive absorbance values (log ΔA) vs time is equal to -k'/2.303. This method gives good results even if methylene green is used without further purification (Fig. 2). In the reaction the plot of log A vs time was linear showing the pseudo first order rate coefficients obtained by slope are 1.6×10⁻³ s⁻¹ and 3.4×10⁻³ s⁻¹ with respect to dye and glucose. Table 1 showed that oxidation of glucose depends upon the concentration of the glucose while

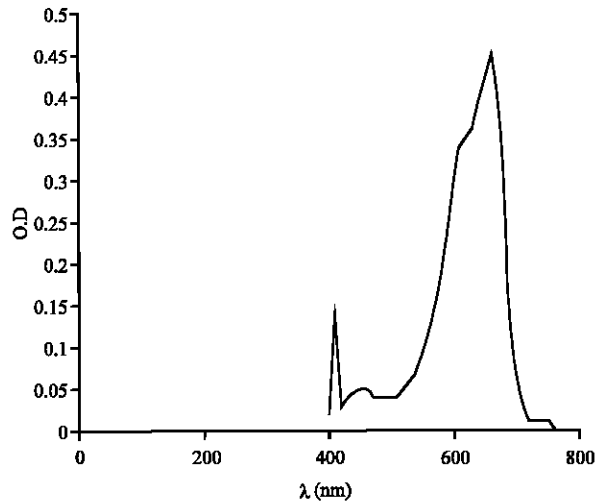


Fig. 1: Absorption spectrum of methylene green in aqueous medium

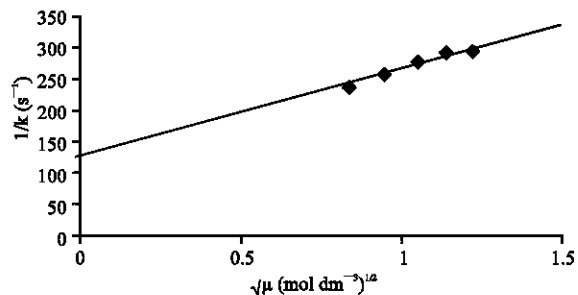


Fig 2: The plot of 1/k vs √μ (ionic strength) for methylene green catalyzed oxidation of D-glucose

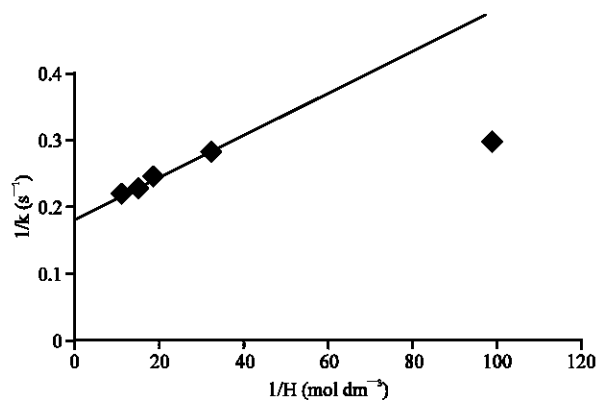


Fig. 3: The plot of 1/k vs 1/H for methylene green catalyzed oxidation of D-glucose

Table 1: Experimental first order kinetics of aerobic oxidation of glucose by methylene green

[MG].10 ⁵ mol dm ⁻³	Glucose.10 ⁴ mol dm ⁻³	NaOH.10 ² mol dm ⁻³	Rate constant k 10 ³ s ⁻¹
0.66	1.66	8.30	1.4
1.33	1.66	8.30	1.5
2	1.66	8.30	1.6
2.5	1.66	8.30	1.6
3.33	1.66	8.30	1.6
0.66	10.00	8.30	3.3
0.66	30.00	8.30	3.4
0.66	50.00	8.30	3.9
0.66	60.00	8.30	4.2
0.66	80.00	8.30	4.4
0.66	1.66	8.30	1.4
0.66	1.66	16.00	1.3
0.66	1.66	25.00	1.2
0.66	1.66	33.00	1.0
0.66	1.66	41.00	0.9

Solvent = Water, Temperature = 30°C, KNO₃ = 0.1 mol dm⁻³

Table 2: Effect of ionic strength on rate of reaction

√μ	10 ³ k. s ⁻¹	1/k	ln k _{obs}
0.836	4.2	238.09	-5.47
0.946	3.9	256.41	-5.54
1.048	3.6	277.77	-5.62
1.140	3.4	294.11	-5.68
1.224	3.4	294.11	-5.68

[MG⁺] = 0.66×10⁻⁵ mol dm⁻³, [RH] = 0.01 mol dm⁻³, [NaOH] = 0.083 mol dm⁻³, Solvent = Water, Temperature = 30°C

Table 3: Effect of Temp on rate of reaction at different ionic strength

√μ	10 ³ .k s ⁻¹				
	Temperature (K°)				
	303	308	313	318	323
0.836	4.2	8.3	9.4	11.3	14.3
0.946	4.7	8.5	9.5	11.5	14.3
1.048	4.5	8.3	9.8	11.6	14.5
1.140	4.3	8.5	9.6	11.7	14.9
1.224	4.3	8.5	9.5	11.6	14.7

[MG⁺] = 0.66×10⁻⁵ mol dm⁻³, [RH] = 0.01 mol dm⁻³, [NaOH] = 0.083 mol dm⁻³, Solvent = Water

independent upon the concentration of the dye. The methylene green catalyzed oxidation of D-glucose in

Table 4: Thermodynamics and Activation Parameters at different ionic strength

√μ	E _a (KJ mol ⁻¹)	ΔH* (KJ mol ⁻¹)	ΔS* (JK ⁻¹ mol ⁻¹)	ΔG* (KJ mol ⁻¹)
1.224	28.76	26.24	-39.24	14.14
1.140	18.07	15.56	-42.56	14.09
1.048	15.73	13.21	-43.22	14.47
0.948	15.72	13.20	-42.31	14.86

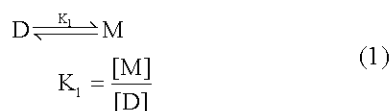
[MG⁺] = 0.66×10⁻⁵ mol dm⁻³, [RH] = 0.01 mol dm⁻³, [NaOH] = 0.083 mol dm⁻³, Solvent = Water

aqueous solvent results in faster bleaching of the dye to more reactive β anomer present in the polar water solvent (Fig. 3). The well known anomeric effect is the energetic favoring of the α anomer in the carbohydrate over the β anomer in mutarotational mixture of anomers.

Effects of change in ionic strength were studied by experiments with varying initial concentration of KNO₃ at constant concentration of MG⁺ and RH. The ionic strength was varied by 0.836 and 1.136 mol dm⁻³. A plot of log/k vs μ^{0.5} is linear with a slope of 1.9 Z_A Z_B. The sign of the slope indicates whether the species involved in the rate determining steps have like or unlike charges and the magnitude gives the product of charges on the species. Since ionic strength influences the reaction rate between charged species significantly. It was found that salt did not affect the reaction time to any significant extents (Table 2). The rate of reactions between two uncharged molecules or between an ion and a molecule are usually only slightly affected by the addition of salt (Table 2). This indicated that primary and secondary salt effects are operative in opposite direction.

Effect of temperature on rate of reaction showed that rate of reaction increases with the increase in the temperature (Table 3). The values of rate constant at different ionic strength with constant temperature showed that rate of oxidation increase with the increase in temperature but the change in ionic strength with change in temperature has no appreciable effect on oxidation. The value of energy of activation for the reaction between methylene green and D-glucose in alkaline medium is 15.78 KJ mole⁻¹ at ionic strength of 1.048 mol dm⁻³ which is comparable with the value of 15.73 KJ mole⁻¹ reported by Snehalatha *et al.* (1997). The value indicated that carbohydrate is oxidized most rapidly existing in aqueous solution predominantly as the β-pyranose anomer (equatorial OH⁻). The value of entropy of activation (ΔS*) given in Table 4 is 39.24 J K mol⁻¹ at ionic strength 1.224 mol dm⁻³ comparable with the value 33.7 and 34.6 J K mol⁻¹ reported by (Uddin, 2000) in acidic medium. The values of ΔH* and ΔG* also show the fast reaction between dye and glucose molecule involving hydrogen abstraction from aldehydic group of glucose molecule.

Mechanism: Reaction mechanism (Snehalatha *et al.*, 1997) involves the interaction in between protonated form of methylene green and glucose molecule. Since $[\text{OH}^-]$ is greater (Cook *et al.*, 1994) therefore oxidation of glucose may take place at the same time. Protonation (MGH) of methylene green also take place and leuco methylene green is formed.



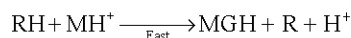
Where K_1 is equilibrium constant in between the two form of methylene blue. Protonation of the dye may take place in solvent



Protonated form of the methylene green may interact with the reductant molecule to form leuco dye.



$$K_3 = \frac{[MGH][\bar{R}]}{[MH^+][RH]} \quad (4)$$



The rate law for the reaction

$$\frac{-d[MG]}{dt} = r = k_2[MH^+][RH] \quad (5)$$

The triplet transition state of the dye

$$\begin{aligned} [MG]_T &= [D] + [M] + [MH] \\ [MG]_T &= M/K_1 + [M] + [MH^+] \end{aligned} \quad (7)$$

or in from of protonated state $[MH^+]$ of the dye
or

$$[MG]_T = [MH^+] + \frac{[MH^+]}{K_2[H^+]} + \frac{[MH^+]}{K_1K_3[H^+]} \quad (8)$$

or

$$[MG]_T = MH^+ \frac{1 + K_1 + K_3K_1[H^+]}{K_1K_3[H^+]} \quad (9)$$

Protonated form of the dye will be

$$[MH^+] = \frac{K_1K_3[H^+][MG]_T}{1 + K_1 + K_3K_1[H^+]} \quad (10)$$

The rate law for the above reaction after substitution of $[MH^+]$ in Eq. 5

$$\frac{d[MG]}{dt} = \frac{K_2K_1K_3[MG]_T[RH][H^+]}{1 + K_1 + K_3K_1[H^+]}$$

The rate law shows first order dependence of RH and fractional order with respect to H^+ .

The above rate law is also verified the first order kinetics. This showed the dependence on the concentration of glucose. The above equation can be written for dimeric form of methylene green in solution:

$$K'' = \frac{K_2K_1K_3[H^+]}{1 + K_1 + K_3K_1[H^+]}$$

$$\text{where } K'' = \frac{-d[MG]_T/dt}{[RH][MG]_T}$$

or inverse of the above equation

$$\frac{1}{K''} = \frac{1}{[H^+]} \frac{1}{k_2K_1K_3} + \frac{1}{k_2K_3} + \frac{1}{k_2}$$

The plot $1/k$ vs $1/[H^+]$ was found to be linear with positive slope having of ($R^2 = 0.6251$) and value of $1/k_2 = 3.03 \times 10^{-3} \text{ s}^{-1}$ showing first order kinetics dependence on reductant concentration.

REFERENCES

- Adamcikova, L., K. Pavlikova and P. Sevcik, 1999. The methylene blue-D-glucose-O-system. Oxidation of D-glucose in the presence and absence of oxygen. *Intl. J. Chem. Kinetics*, 31: 463-468.
- Adamcikova, L., M. Hupkova and P. Sevcik, 2000. Pattern formation in the methylene blue-fructose-oxygen system in aqueous solution and in gel system. *Collection of Czechosland. Chem. Comm.*, 65: 1394-1402.
- Cook, A.G., R.M. Toliver and J.E. Willams, 1994. The blue bottle experiment revisited. *J. Chem.*, 71: 160-161.
- De Lucca, A.R., S.A. Santos, A.C. Pereira and L.T. Kubota, 2002. Electrochemical behavior and electro catalytic study of the methylene green coated on modified silica gel. *Interface Sci.*, 254: 113-119.

- Jonnalagadda, S.B. and N.R. Gellapalli, 2000. Kinetics of reduction of toluidene blue with sulfite. Kinetics salt effect in elucidation of mechanism. *J. Chem. Edu.*, 77: 506-508.
- Kamat, P.V. and N.N. Lichtin, 1982. Electron transfer in the quenching of protonated triplate thionine and methylene blue by ground state thionine. *J. Photochem.*, 18: 197-209.
- Liu, Y., S. Yamamoto, Y. Fujiyocna and Y. Sueishi, 2000. Kinetic study on the reversible hydride transfer between methylene blue and thionine. *Phys. Chem. Chem. Phys.*, 2: 2367-2371.
- Liu, Y., S. Yamamoto and Y. Sueishi, 2001. Photos induce hydride transfer reaction between methylene blue and leuco crystal violet. *J. Photochem. Photobiol. Chem.*, 143: 153-159.
- Mowry, S. and O. Paul, 1999. Kintics of methylene blue reduction by ascorbic acid. *J. Chem. Edu.*, 76: 970-974.
- Quitevis, E.L., J. Martorell, Y. Chang and T.W. Scott, 2000. Photo reduction of Methylene blue on cadmium sulfide powder. *Chem. Phy. Lett.*, 319: 138-144.
- Snehalatha, T., K.C. Rajanna and P.K. Salprakash, 1997. Methylene blue ascorbic acid. *J. Chem. Edu.*, 74: 228-233.
- Uddin, F., 2000. Kinetics of photochemical reactions of thionine with thiourea. *Eur. J. Org. Chem.*, 2: 1345-1351.
- Uddin, F., Q.Z. Hasnain and M.Y.K. Yousuf Zai, 2001. Photo reduction of thiazine dye with trimethyl amine. *Arab. J. Sci. Eng.*, 26: 109-175.
- Uddin, F. and Q.Z. Hasnain, 2002. Photochemical reduction of thionine with dimethyl amine. *Kuwait J. Sci. Eng.*, 29: 67-85.