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Kinetics of Methylene Blue Reduction with Oxalic Acid by Visible Spectrophotometric Method

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The redox reaction between methylene blue (MB) and oxalic acid was followed qualitative interpretation and spectrophotometrically for quantitive determination. This investigation compares spectrophotometric studies of MB^+ reduction by oxalic acid at acidic pH. The colour loss of MB^+ was observed at 668 nm showed that the reaction follows identical kinetics with respect to dye, reductant and HCl. The slow reaction with oxalic acid was observed in absence of acid. Regeneration of MB^+ colour by reaction with dissolved oxygen of atmosphere was observed. The effect of change in ionic strength shows no significant change to extent of reaction. Reaction effected by change in temperature and activation parameters were computed. A mechanism consistent based on above conclusion has also been proposed.

Key Words: Kinetics, Methylene blue, Oxalic acid, pH.

INTRODUCTION

Reactions of thiazine dyes such as methylene blue (MB), methylene green and toluidene blue with different reducing agents had been widely studied since its time of synthesis in 1876[1-7]. The reduction of methylene blue exhibits complex kinetics. Depending on the reductants, these reactions follow varying orders with respect to the reductant which is either first-order or fractional-order dependence[1,2] on MB^+. Methylene blue is easily reduced to the colourless hydrogenated molecule, leuco methylene blue by a variety of reducing agents, which can be oxidized back to blue colour[3]. The bleaching of methylene blue with ascorbic acid in presence of acidic medium was reported by Snehalatha *et al.*[4] at different ionic strength; The negligible salt effect [K_2SO_4 + KCl] was found that salt did not affect the reaction time to any significant extent. Photo induced hydride transfer reaction between methylene blue (MB^+) and leuco crystal violet (CVH) by visible light was found that irradiation of solution of MB^+ and CVH shows the disappearance of MB^+ and formation of (CV^+) simultaneously[5]. The

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photochemical reduction of thiazine with trimethylamine and dimethylamine shows that quantum yield of reduction processes depend upon the concentration of reductant, acidity and temperature of the reaction mixture while it is independent upon the concentration of dye[6,7].

The kinetics of hydride transfer reaction between leucomethylene blue (LMB) and thionine (TH) shows pseudo first order reaction[8]. The complex mechanism in between LMB and TH were reported.The reduction of methylene blue by various reductants like cadmium sulfide, amines followed by triplet transient of MB[9-15].

In the present study the reaction between methylene blue and oxalic acid was followed by visible spectrophotometric technique in acidic medium. The reduction of methylene blue will be investigated at different experimental conditions such as change in concentration of dye, reductant, ionic strength, H^+ ion and temperature. An attempt will be made to propose a mechanism based on investigation.

EXPERIMENTAL

Methylene blue, oxalic acid, hydrochloric acid of E. Merck were used. The stock solution of dye (1×10^{-4} mol dm^{-3}) was prepared in conductivity water and preserved in polyethylene bottles. The oxalic acid and hydrochloric acid were used without further purification .

Kinetics measurements

Three sets of mixtures were prepared from stock solution. In each set one species was varied while other two were kept at fixed initial concentration. In all sets the concentration of MB^+ was less than 1 % of the acid and oxalic acid. The three contents were mixed together and portion was transferred to the cuvette (1.00 con) to record a change in optical density of methylene blue.

Kinetic measurements were made with visible spectrophotometer at λ_{max} 668 nm of methylene blue. Kinetics runs were made at time intervals of 200 to 400s depending on the specific reaction rates. Ordinary light levels had no observable effects on rate of reaction.

RESULTS AND DISCUSSION

The dye reduction processes were investigated at different initial concentrations of dye, reductant, HCl, ionic strength of the medium and temperature.

The concentration and experimental first order decay constant for several runs were reported in Table-1. The plots of ln $(A_O - A_\alpha)/(A_t - A_\alpha)$ (A_O absorbance at time 0, A_t absorbance at time t where t_α is absorbance at infinite time) for first-order decay plots for several concentration of $MB^+_{(OX)}$

under constant initial concentration of HCl and oxalic acid molarities are shown in Fig. 1. The slopes of the lines were the k_{exp} values, this shows that dye reduction processes was independent upon the initial concentration of methylene blue. The rate of reaction does not alter with the change in the concentration of methylene blue with constant concentration of HCl and oxalic acid. The results showed that rate of reduction were independent upon the concentration of methylene blue.

TABLE-1
EXPERIMENTAL FIRST ORDER KINETICS OF METHYLENE BLUE REDUCTION BY OXALIC ACID AT 30ºC

[HCl] = 1 × 10^{-1} mol dm^{-3} [Oxalic acid] = 1 × 10^{-3} mol dm^{-3}		[MB] = 1 × 10^{-5} mol dm^{-3} [Oxalic acid] = 1 × 10^{-3} mol dm^{-3}		[MB] = 1 × 10^{-5} mol dm^{-3} [HCl] = 1 × 10^{-1} mol dm^{-3}	
[MB] mol dm^{-3} × 10^{5}	k_{obs} s^{-1} × 10^{2}	[HCl] mol dm^{-3} × 10^{1}	k_{obs} s^{-1} × 10^{2}	Oxalic acid mol dm^{-3} × 10^{2}	k_{obs} s^{-1} × 10^{2}
1.0	3.2	1.0	5.1	1.0	2.0
2.0	3.2	2.0	5.5	1.5	2.1
3.0	2.9	3.0	6.5	2.0	2.3
4.0	3.1	4.0	7.3	3.0	3.0
5.0	3.1	5.0	8.6	4.0	3.2
7.0	3.2	6.0	8.9	5.0	3.5
9.0	3.2	7.0	9.1	6.0	4.1

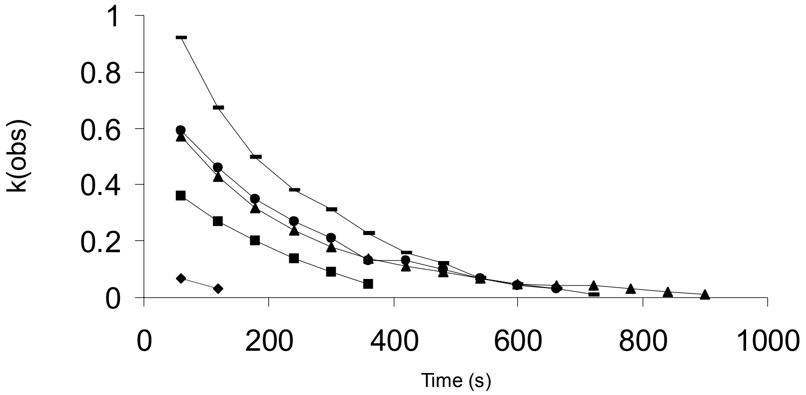


Fig. 1. First order decay plots for MB^+ absorbance at 668 nm with constant [oxalic acid] and [HCl]

Similar plots were used to obtain k_{exp} values for all sets of experiment. Figs. 2 and 3 show that rate constant k_{exp} depend upon the concentration of oxalic acid and HCl. These graphs also suggest that rate of reaction followed first order kinetics with respect to HCl and oxalic acid concentration. Dye reduction process was also observed in absence of HCl. In the light of above facts the rate law comes out to be.

$$\frac{d[MB^+]}{dt} = \{k_O + k_1[H^+][AH_2][MB^+]\}$$

$$= \frac{-d[MB^+]}{dt} = k_{exp}[MB^+]$$

or, $r = K$ [Oxalic acid][MB^+]

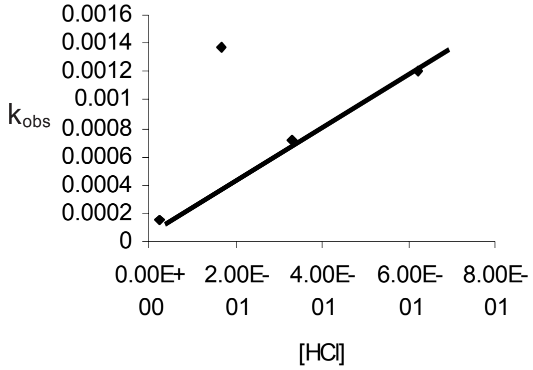


Fig. 2. k as a function of [HCl] slope = 0.36 and intercept = 0.00019

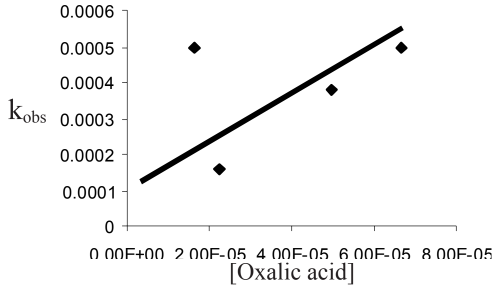


Fig. 3. k_{obs} as a function of reductant (oxalic acid) slope = 2.5 mol dm^{-3} s^{-3}

The bleaching of MB^+ with oxalic acid in absence of HCl was much slower as compared to the runs with HCl and absorbency reaches to zero in about 5 min. The visible spectrum was due to MB^+ during all runs of sets. The dissolved oxygen may play significant role in the system under study. The reduction of MB^+ by oxalic acid in acid medium proceeded by a complex mechanism[9,10]. However, the kinetics data would also be consistent with second order reaction of oxalic acid and methylene blue. The reaction with oxaic acid requires a net transfer of two H^+ and $2e^-$.

Since, ionic strength contribution of HCl is already high in these studies and thus further increases due to additional salts produce no significant effect on MB^+ reduction rates[3]. Kinetics electrolyte effects are usually referred to as kinetic salt effects. Results of the present study appear to be in agreement with a mechanism in which primary and secondary salt effect are operative in opposite directions. However, the participation of ion-dipole or dipole-dipole in the slow step could not be ruled out. Fig. 1 shows that the observed negative kinetics salt effect suggests that the rate-limiting step of the reaction is hydrogen abstraction and electron transfer reaction takes place.

$$2MB^{+} + C_2O_4H_2{\cdot}2H_2 \xrightarrow{H^{+}} \underset{\text{Complex}}{[MB^{+}\text{----}C_2O_2\text{----}H_2]} \qquad 2MBH + C_2O_4^{2-}]$$

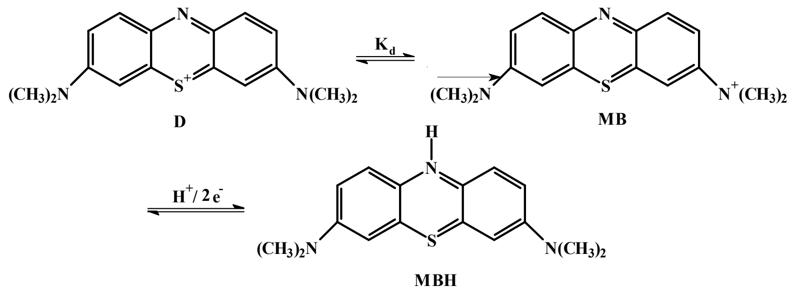
Mechanism of the reduction

Methylene blue reduced to leuco dye by oxalic acid in presence of acidic medium. Oxalic acid exists in $C_2O_4^{2-}$ and $2H^{+}$-ion state and equilibrium is established in dissociated and undissociated state.

$$(COOH)_2{\cdot}2H_2O \rightleftharpoons 2C_2O_4^{2-} + 2H^{+}$$

Reaction is highly favorable in acidic concentration, therefore it is reasonable to consider that undissociated reacted species $(COOH)_2{\cdot}2H_2O$ (AH_2) is the reactive species.

In acidic medium MB exists as follows:



(1)

where K_d is the equilibrium in between two state of methylene blue. Experimental findings suggest that first order dependence on reductant, MB dye and HCl with no appreciable salt effect due to higher H^{+} concentration.

$$AH_2 + H^{+} \overset{k_1}{\rightleftharpoons} (AH_3)^{+} \qquad (2)$$

$$(AH_3)^{+} + MB \xrightarrow[\text{slow}]{k} MBH + AH^{+} + H^{+} \qquad (3)$$

$$AH + MB \xrightarrow[\text{fast}]{} MBH + A \qquad (4)$$

The rate law for above reaction

$$\text{Rate law } \frac{-d[MB]}{dt} = k[MB][AH_3]^{+} \qquad (5)$$

From equilibrium

$$[MB] = K_d\,[MB] \text{ or } [D] = \frac{[MB]}{K_d}$$

$$[MB]_T = [D] + [MB] \text{ or } [MB]_T = MB\,\frac{K_d + 1}{K_d}$$

$$[MB] = \frac{K_d[MB]_T}{(1 + K_d)} \qquad (6)$$

According to equation (2)

$$[AH_2]_T = [AH_2] + [AH_3]^+$$

$$K_1 = \frac{[AH_3]^+}{[AH_2][H^+]}$$

or $$[AH_2] = \frac{[AH_3^+]}{K_1[H^+]}$$

$$[AH_2]_T = [AH_3^+] + \frac{[AH_3^+]}{K_1[H^+]}$$

$$[AH_2]_T = [AH_3^+]\frac{1 + K_1[H^+]}{K_1[H^+]}$$

$$[AH_3^+] = \frac{K_1[H^+][AH_2]_T}{1 + K_1[H^+]} \qquad (7)$$

Substitution of $[AH_3^+]$ and [MB] in equation (5) gives

$$\frac{-d[MB]}{dt} = v = \frac{kK_dK_1[MB]_T[AH_2]_T[H^+]}{\{1 + K_1[H^+]\}\{1 + K_d\}} \qquad (8)$$

This equation explains the observed kinetics with the help of proposed mechanism: The above rate equation may be simplified as follows:

$$K'' = \frac{kK_dK_1[H^+]}{[1 + K_1[H^+]][1 + K_d]} = \frac{k_1K_1[H^+]}{1 + K_1[H^+]}$$

where $$K'' = \frac{-d[MB]/dt}{[AH_2]_T[MB]_T} \qquad (10)$$

$$k_1 = k\frac{K_d}{1 + K_d}$$

reciprocal of above equation gives

$$\frac{1}{k} = \frac{1}{k_1K_1[H^+]} + \frac{1}{k_1} \qquad (11)$$

Eqn. 11 shows that the plots of 1/k and $1/H^+$ should be linear with positive slope and intercept.

The rate constants (k_1) were determined at various temperatures in acidic medium and activation parameters E_a, ΔH^*, ΔG^* and ΔS^* were computed in Table-2 and calculated by using Arrhenius and Erying equations.

TABLE-2
THERMODYNAMIC ACTIVATION PARAMETERS
[HCl] = 1 × 10^{-1} mol dm^{-3} [MB] = 1 × 10^{-5} mol dm^{-3}, [Oxalic acid] = 1 × 10^{-3} mol dm^{-3}

E_a	ΔH*	ΔG*	ΔS*
18.21 KJ mol^{-1}	25.20 KJ mol^{-1}	10.30 KJ mol^{-1}	40.23 J K^{-1} mol^{-1}

Conclusion

The reaction between methylene blue and oxalic acid follows first order kinetics with respect to dye concentration and reductants in presence of atmospheric oxygen in acidic medium and rate of reduction was slow in the absence of acid.

REFERENCES

1. S.B. Jonnalagadda and N.R. Gellapalli, *J. Chem. Edu.*, **77**, 506 (2000).
2. K.J. Laidler, Reaction Kinetics, Reaction in Solution, Pergamon Oxford, Vol. 2, p.18 (1965).
3. S. Mowry and P.J. Organ, *J. Chem. Edu.*, **76**, 970 (1999).
4. T. Snehalatha, K.C. Rajanna and P.K. Salprakash, *J. Chem. Edu.*, **74**, 228 (1997).
5. Y. Liu, S. Yamamoto and Y. Sueishi, *J. Photochem. Photobiol. A Chem.*, **143**, 153 (2001).
6. F. Uddin, Q.Z. Hasnain and M.Y.K.Y. Zai, *Arab. J. Sci. Eng.*, **26**, 109 (2001).
7. F. Uddin and Q.Z. Hasnain, *Kuwait J. Sci. Eng.*, **29**, 67 (2002).
8. Y. Liu, S. Yamamoto, Y. Fujiyocna and Y. Sueishi, *Phys. Chem. Chem. Phys.*, **2**, 2367 (2000).
9. F. Uddin, *Eur. J. Org. Chem.*, **2**, 1345 (2000).
10. P.V. Kamat and N.N. Lichtin, *J. Photochem.*, **18**, 197 (1982).
11. E.L. Quitevis, J. Martorell, Y. Chang and T.W. Scott, *Chem. Phys. Lett.*, **319**, 138 (2000).
12. K. Kikuchi, S.T. Tamura, C. Iwanaga, H. Kokubun and Y. Usui, *Z. Phys. Chem.*, **106**, 17 (1977).
13. L.V. Romashov, I.Y. Kiryukhion and K.S.B. Yen, *Dokl. Phys. Chem.*, **230**, 961 (1976).
14. R.H. Kayser and R.H. Young, *Photochem. Photobiol.*, **24**, 395 (1976).
15. S. Kato, M. Morita and M. Koizumi, *Bull. Chem. Soc. (Japan)*, **37**, 117 (1964).

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