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Full Length Research Paper

Kinetics of proton depended oxidation of diethylthiourea with methylene green in aqueous medium

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Diethylthiourea (DETU) reacts with methylene green (MG) and reduced it into leuco dye where it oxidized into smaller fragments like urea, nitrate and sulphate. The reaction was favorable in acidic condition. A direct relation in between oxidation of DETU and MG to the concentration of H^+ ions was observed through typical kinetics in two acids like HCl and H_2SO_4. The second order with respect to HCl and the first order with respect to H_2SO_4 indicated the protonation of DETU with the reduction of dye. In alkaline medium, the rate of reaction decline may be due to the suppressing effects of alkali on oxidation/degradation of DETU into smaller fragments or may be attributed with the de-protonation of DETU. Influence of addition of dye into reaction mixture retarded the bleaching process and follows zero order kinetics while rate of reaction enhanced by the addition of DETU in the reaction mixture and shows ¾th order with respect to DETU. Negative effect of added different electrolytes reflects that change of ionic strength of reaction mixture have some bearing on redox reaction of MG and DETU. Reaction was monitored at elevated temperature and activation parameters were computed. The mechanisms of oxidation of DETU with reduction of dye MG were discussed. Reduction of MG into leuco dye with the fragmentation of DETU was observed in acidic condition at elevated temperature.

Key words: Methylene green (MG), diethylthiourea (DETU), proton dependence, smaller fragments, redox reaction, ions.

INTRODUCTION

Irradiation of the fluorescent dyes in their visible absorption bands excites metastable triplet states which decay by the bimolecular reaction of triplet molecules. A rapid reaction of phenol with triplet eosin is shown by the retardation of the rate of aerobic photobleaching and an acceleration of the rate of triplet disappearance (Bujdák, and Nobuo, 2002; Rauf et al., 2008).

Our interest in dye chemistry has been to understand the role of dyes molecules with various reductants in dye bleaching as well as in the oxidation of reductant. Our successive studies on the reduction of thiazine dye by various reductants, like ribose (Azmat and Uddin, 2009), thiourea (Uddin, 2009), galactose and D-mannose (Azmat and Uddin, 2000; Ahmed et al., 2009), monomethylamine (Uddin and Hasnain, 2006), triethylamine (Uddin et al., 1998), trimethylamine (Uddin et al., 2001), dimethyl amine (Saeed and Uddin, 2006; Uddin and Hasnain, 2002), urea (Ahmed et al., 2010), methylamine and ethyl amine (Saeed et al., 2004), N-Phenylglycine (Uddin, 1996) revealed the consistent pattern of electron transfer and hydrogen abstraction via triplet transition state in inert atmosphere (Khalid et al., 2008).

In this paper, we report the oxidation of diethylthiourea (DETU) with methylene green in aerobic condition not reported yet to the best of our knowledge. Rábai et al. (1993) reported that in high acid and excess ClO_2, thiourea is oxidized to relatively stable formamidine sulfinic acid {[(NH)(NH_2)CSO_2H]} with decreasing pH, the rate increases and the disappearance of ClO_2 becomes autocatalytic. Typical kinetics was observed when thiourea was oxidized with potassium dichromate (Rao,

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1970) and oxidation was proceeding to via addition of oxygen when reaction was monitored by bromate in acidic medium (Simoyi et al., 1994; Olagunju et al., 2006).

This paper covers the bleaching of dye in relation with the oxidation of DETU in two acids environment, alkali, and other operational parameters to propose the mechanism of redox reactions. The kinetics parameters and mechanistic details of redox reaction will show how the reaction represents the most important oxidation of DETU under influences of various ions like NO_3^-, SO_4^{2-}, Cl^-, Br^- and I^-.

MATERIALS AND METHODS

All reagents from E-Merck were used as received. The experiment was divided into different sessions, including preparation of solutions, kinetic measurements, data analysis and investigation of kinetic salt effect. All solutions were prepared in de-ionized water and diluted before use. Kinetics was monitored on a UV/visible Schimadzu 160A spectrophotometer.

Preparation of sample solutions

MG stock solution of 1×10^{-4} mol.dm^{-3} was prepared in 250 ml of de-ionized water. Dilutions of this stock solution were made with de-ionized water to obtain a series of dye solutions with varying concentrations of reagents as indicated in the Tables.

Kinetics measurements

Kinetics was monitored by preparing three sets of reaction mixtures in which one specie was varied while other two were kept constant, namely, dye, reductant, acid or base (Azmat et al., 2007). The three contents were mixed together and the progress of the (inlet) reaction was monitored by recording the change in optical density with time at λ_{max} = 652.8 nm on the UV/visible spectrophotometer. The absorbance value monitored in each case was plotted against time to obtain rate constant. The orders of reaction and activation parameters were evaluated by measuring the specific reaction rate at various temperatures and ionic strengths (Abdelghani et al., 2001; Azmat et al., 2006). Potassium chloride (KCl) and potassium bromide (KBr) were used to maintain the ionic strength of the medium. Percentage decrease in absorbance was calculated using the formula:

$$\text{Decrease in absorption (\%)} = \left(1 - \frac{A_f}{A_i}\right) \times 100$$

where A_f = absorbance after 15 min or final absorbance. A_i = absorbance at 0 min or initial absorbance.

High performance liquid chromatography (HPLC) analysis of the decolorized mixture

The HPLC analysis of a mixture of dye was carried out by the method described by Ahmed et al. (2010). The C_8-Eclips columns (Agilent) with the dimension of 4.6 × 250 mm and injection volume is 20 µl using 0 to 100% methanol (water as the base mobile phase) gradient over 30 min at 1 ml/min and analyzed by measuring the optical density (OD) at wavelength of 280 nm (Ahmed et al., 2010).

Stiochometric ratio

For the determination of stiochiometric ratio of MG with DETU, reactants were mixed in molar ratios of 2:1, 1:1 and 1:2 with HCl, H_2SO_4 and NaOH in excess. The mixtures were left for 24 h in the dark. The residual reactant mixtures were analyzed by time to time (2 h). MG was found to react with DETU in 1:2 ratios. The reaction was rapid in H_2SO_4 while slow in HCl, whereas totally inhibited in alkaline medium (Ahmed et al., 2010).

The overall reaction may be represented as follows:

$$MG + 2DETU \xrightarrow[H_2SO_4]{2H^+} MGH_2 + Secondary \quad product$$

$$MG + 2DETU \xrightarrow[HCl]{H^+} 2MGH + Secondary \quad product$$

$$\text{MG} + \text{2DETU} \underset{\text{NaOH}}{\overset{\text{OH}^-}{\rightleftharpoons}} \text{MG} + \text{Non Reactive Fragments}$$

Qualitative analysis of reaction mixture

Qualitative test of reaction mixture containing thiourea and dye were performed for the determination of different oxidative components after decoloration of mixture.

Test for carbonyl (C=O) functional group

Add 2,4 dinitrophenyl hydrazine to the reaction mixture in alcohol and reflux the mixture. Light yellow orange precipitate is obtained on cooling which indicates the presence of carbonyl (C=O) group.

Test for urea

The violet coloration was obtained when reaction mixture was heated, dissolved in NaOH and add one drop of dilute H_2SO_4.

Test for thiocyanates

A pinch of Zn dust with 2 ml of dilute HCl was added in the reaction mixture and boils, and then it was filtered. Green precipitate was obtained when 3 to 4 ml of concentrated NaOH was added with freshly prepared $FeSO_4$ solution in the filtrate. 1.0 ml of HCl was added in green precipitate, after heating. Prussian blue coloration of ferric ferocynide was obtained as:

$$\underset{\text{Thiocyanate}}{R.SCN} + 2H \xrightarrow{Zn+HCl} \underset{\text{Mercaptane}}{R.SH} + HCN$$

$$HCN + NaOH \longrightarrow NaCN + H_2O$$

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{Dirty green ppt.}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow Na_4Fe(CN)_6 + 2NaOH$$

$$\underset{\text{Sodium ferrocyanide}}{3NaFe(CN)_6} + 2Fe_2(SO_4)_3 \longrightarrow \underset{\text{Ferric ferro cyanide (Purssian blue)}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO$$

Table 1. Effect of change in monoprotic and diprotic acid and alkali on decoloration of methylene green (MG).

	$v \times 10^5$ (mol.dm^{-3}.s^{-1})	$k \times 10^4$ (s^{-1})	Decoloration (%)
HCl × 10^2 (mol.dm^{-3})			
3	2.0	0.90	10.47
5	5.0	3.0	28.44
6	7.0	4.0	35.68
7	10.0	7.0	54.55
8	10.0	9.0	59.91
H_2SO_4 × 10^2 (mol.dm^{-3})			
2	10	2	16.93
4	20	4	35.61
6	20	7	49.36
7	20	9	55.84
8	20	10	60.21
NaOH × 10^2 (mol. dm^{-3})			
1	6	4	26.73
3	4	2	16.95
5	5	3	22.51
7	6	3	22.55
8	6	3	22.64

v = Rate of the reaction , k = Specific rate constant.

Test for SO_4^{--}

Small amount (0.Igm) of $BaSO_4$ solution was added to a mixture solution along with 2 to 3 drops of dilute HCl, white precipitate was obtained which was insoluble in dilute HCl in excess, which indicate the presence of SO_4^{--}. Addition of lead acetate to the mixture solution gives white precipitates which confirm the presence of SO_4^{-}

$$SO_4^{2-} + BaCl_2 \longrightarrow 2Cl^- + BaSO_4 \downarrow$$

White ppt

$$SO_4^{2-} + (CH_3COO)_2Pb \longrightarrow 2CH_3COO^- + PbSO_4 \downarrow$$

White ppt

Test for NO_3^{-}

Add concentrated H_2SO_4 to the mixture solution and warm gently. Yellowish brown vapours which intensified on adding Cu turning confirms the presence of NO_3^{--}.

$$2NO_3^- + H_2SO_4 \longrightarrow SO_4^{2-} + 2HNO_3$$

$$\underset{\text{Yellowish Brown Gas}}{4HNO_3} \longrightarrow 2H_2O + O_2 + \underset{\text{Yellowish Brown Gas}}{4NO_2} \uparrow$$

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + \underset{\text{Brown Gas}}{2NO_2} \uparrow$$

Brown Gas

RESULTS AND DISCUSSION

Kinetics measurements

The reactivities of most organosulfur compounds like thiourea involve their oxidations and non linear chemistry, and to several degrees their dimerizations or degradation leads to the non linear kinetics. Redox kinetics measurements of DETU and MG were monitored at different operational parameters which involved effects of H^+ through two acids, that is, monobasic (HCl) and dibasic acids (H_2SO_4). The rates of reaction increases linearly at elevated [H^+]. Results were presented as shown in Table 1 which showed that rate of reactions followed different order with respect to HCl and H_2SO_4. The log [HCl] and log [H_2SO_4] versus log "k" gave linear plots with gradients 2.3 (r^2 = 0.9934) and 1.1 (r^2 = 0.9928), respectively with DETU suggested that the order with respect to HCl was second and with H_2SO_4 was unity which showed the acid dependence catalysis of MG and DETU. The study of the protonation of thiourea showed that, even though both N and S centers are basic, the first proton attaching to thiourea in acidic environments oscillates between these two centers while spending more time on the sulfur center. The protonation of the amino groups, though feasible, has no consequence on the reactivity of this molecule (Rábai et al., 1993; Rao, 1970; Simoyi et al., 1994; Olagunju et al., 2006).

The experimentally observed acid dependence oxidation

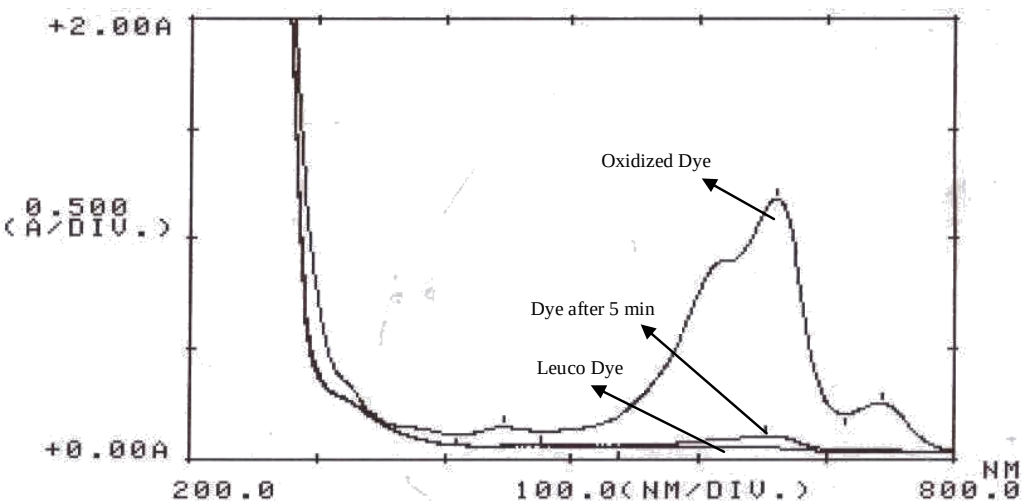
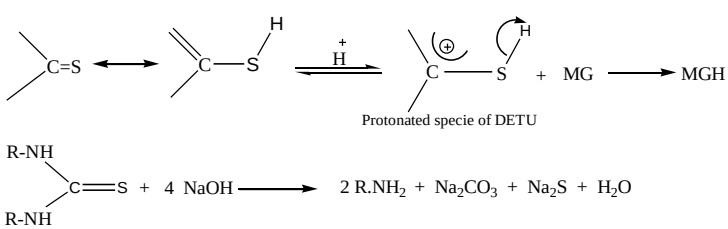


Figure 1. Bleaching of MG with DETU in the presence of HCl medium.

and reduction can now be explained by an increase in concentration of both acids which results in an increase in rate constant "k", while no appreciable changes in the rate constant in alkali showed that protonation of DETU was significant for the reduction of dye (Table 1) and it could be the slow rate determining step where the dye can abstract the proton to form the leuco dye according to following step (Simoyi et al., 1994).



The spectral changes (Figures 1 and 2) recorded in the presence of both acids support the fact that the dye reduced in the presence of reductant in an acidic environment without shift in wavelength, which indicate the formation of MGH. The decline effect of alkali on thiourea oxidation and dye reduction may be related with the de-protonation DETU due to which reactive urea specie was not generated, which commonly acts as strong reducing agent for dye reduction**.**

Influence of addition of dye and reductant into reaction mixture were tabulated in Table 2. According to Table 2, the rate of dye bleaching retarded with the incremental concentration of dye and enhanced by the addition of DETU. The reaction followed zero order kinetics with respect to dye, while $3/4^{th}$ order with respect to reductant showed that the rate of reaction depend on the concentration of DETU (Uddin 2000). This showed the possibility of complex formation since the concentration of the complex expected more at higher concentration of reductant, but further increase in concentration showed no effect on rate, which may be due to the fragmentation of thiourea or dye, as percentage bleaching increases with the increase in concentration of DETU (Table 2). It was found out that the response of methylene green decoloration was very sensitive to the independent factors of dye concentration, DTEU concentration and acid base concentrations. It is apparent from Table 2 that there is a completion in redox reaction, that is, energy transfer from the excited dye sensitizer to atmospheric oxygen and substrate. The efficiency of each process depends upon the concentration of the reactant as well as rate constant of the two processes.

Influence of various electrolytes

The efficiency of dye sensitized oxidation of DETU depends on the number of factors, such as effects due to anions and cations as an electrolyte, oxidation-reduction process of anions and cations with their charge and size of the electrolyte. Results reported in Table 2 showed that reduction of dye and oxidation of thiourea was markedly suppressed in the presence of SO_4^{2-} ions which have high charged density and large size that could be effective in the decoloration percentage (0.15%). Whereas added Cl^- ion showed highest percentage decoloration which support the significance of size in dye coloration. $H\overset{*}{O}\overset{-}{C}l$ produced a strong bleaching agent for MG (Olagunju et al., 2006).

$$Cl^- + \overset{*}{O}H \longrightarrow H\overset{*}{O}\overset{-}{C}l \quad (1)$$

$$Cl^- + O\overset{*}{H} \longrightarrow H\overset{*}{O}\overset{-}{C}l + H^+ \longrightarrow \overset{*}{Cl} + H_2O \quad (2)$$

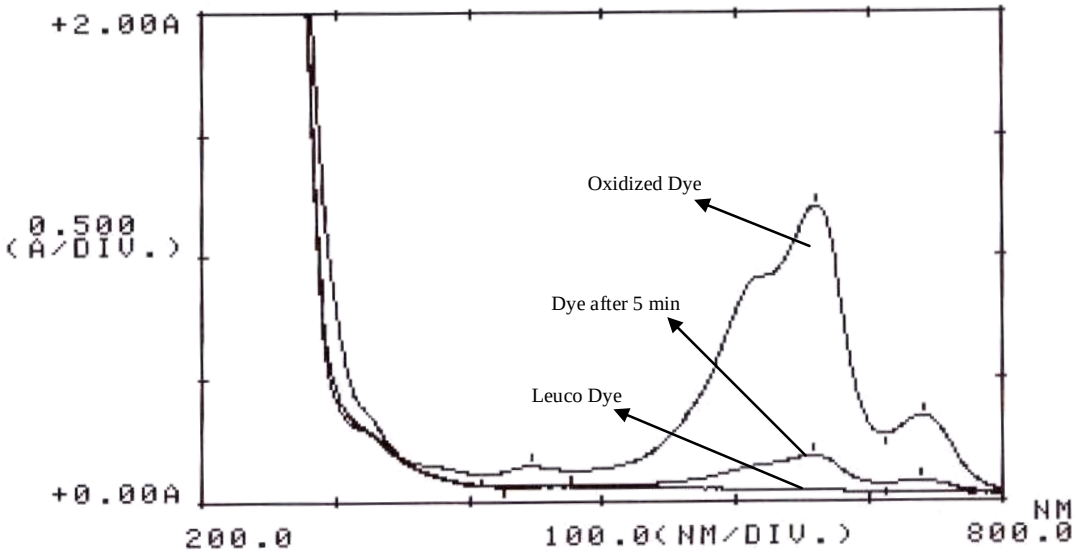
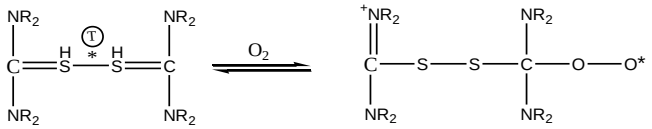


Figure 2. Bleaching of MG with DETU in the presence of H_2SO_4 medium.

Table 2. Effect of change in anions/cations on rate of reduction of MG with DETU.

	$v \times 10^5$ (mol.dm^{-3}.s^{-1})	$k \times 10^4$ (s^{-1})	Decoloration (%)
Anion			
Cl^-	10	3	24.61
Br^-	9	2	18.66
I^-	10	2	20.69
NO_3^-	10	3	20.46
SO_4^{--}	0.1	0.01	0.15
Cation			
Na^+	10	3	20.57
K^+	10	3	24.61
Ca^{++}	5	3	3.21
Mg^{++}	8	1	9.42
Al^{+++}	10	2	10.88

By comparing the data with those in the absence of salt, the results have been interpreted in terms of the condensation of cations around the dimer and the hydration structure of cations (Olagunju et al., 2006). In the presence of anions, such as NO_3^-, SO_4^{2-}, Cl^-, Br^- and I^-, the initial disappearance rate of dye drops which may be due to the oxidation of DETU that involves the successive oxidation of the sulfur center as reported earlier (Rábai et al., 1993; Rao, 1970; Simoyi et al., 1994; Olagunju et al., 2006) or it may be related with the size and charges of anions according to the following equation.



The rate of decolorization was markedly decreased in the reaction mixture containing Ca^{2+} and Mg^{2+} metal ions (Table 2). Investigations showed that the effect of electrolytes on the dye, sensitized redox reaction based on the oxidation state of the cations and anions which have been varied by choosing different electrolytes, such as Na^+, K^+, Cl^-, Br^- and I^- where maximum decoloration was observed, while, in the presence of Ca^{2+}, Mg^{2+} and SO_4^{2-} minimum bleaching rate was observed (Table 3). Highest decoloration was observed in the presence of Cl^- than Br^- , NO_3^- and I^-, may be due to excess electrons which can influence in the formation of semi-reduced dye. It was observed that addition of SO_4^{2-} ion caused a minimum effect on the percentage decolorization of the dye solution. This may be due to the common ion effect on reaction mixture as oxidation of DETU also gives sulphate radical. These results suggested that Cl^- is more

Table 3. Effect of change in concentrations of dye and reductant (DETU).

MG × 10^6 (mol.dm^{-3})	DETU × 10^2 (mol.dm^{-3})	ν × 10^5 (mol.dm^{-3}.s^{-1})	k × 10^4 (s^{-1})	Decoloration (%)
1	0.9	1	0.4	3.43
1	2	3	0.8	6.85
1	5	3	1	9.35
1	6	4	2	12.34
1	7	5	2	13.48
8	1	2	0.6	6.56
9	1	1	0.3	3.95
10	1	2	0.3	2.32
20	1	3	0.3	2.72
30	1	3	0.3	2.41

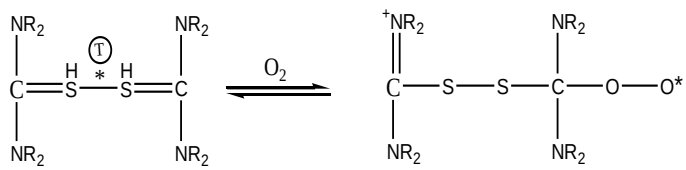
suitable than any other anions, whereas an increase of the concentration of Na^+, K^+, Mg^{2+}, Ca^{2+} and Al^{3+} gives a decrease in decoloration rate. This may be related with high charge-density surfaces induced by the formation of H-aggregates, with a face-to-face association between the dye cations. It was supported by the layer formation in the presence of these ions during experiments which can prevent the entry of photon of light.

Effects of temperature

Reaction was monitored at elevated temperature and activation parameters were computed. It was found that the initial rate of MG depleted with rise in temperature which may be due to the effect of dissolved oxygen, that shifts equilibrium towards reactants side while very high value of ΔG suggest that reaction is non spontaneous and exothermic, or this may be related with thiourea disappearance which increases when temperature of reaction mixture increases (Table 4) as reported by Abdelghani et al. (2001). Activation parameters have been evaluated and a reaction scheme has been proposed postulating a sterically controlled nucleophilic attack of thiourea molecule on half-reduced methylene green radical in the rate limiting step (Jonnalagadda and Dumba 1993). Variations in rates between two acids as shown in Table 1 are caused by change in entropy which is more significant than enthalpy in the free energy barrier to the reaction.

Redox reaction of MG and DETU

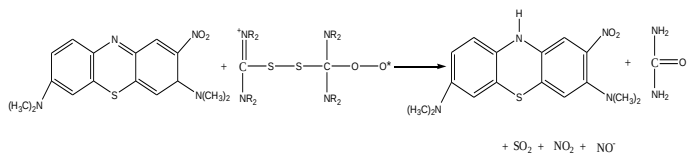
Finally, kinetics of oxidation of DETU photomineralization*$^+$ to urea, nitrate and sulfate and reduction of MG were established. The redox reaction of DETU with MG is a complex free radical chemistry which is very different from that exhibited by carbon centered free radicals (Simoyi et al., 1994; Olagunju et al., 2006). Thioureas are powerful bleaching agents commonly used in dye industry and formed through three-electron-bonded intermediates, such as $RSS\overset{*}{R}^{-}$, $R_2SS\overset{*}{R}_2^{+}$ or R_2SOH (Simoyi et al., 1994). It was assumed that dye sensitized singlet oxygen was involved in the formation of per oxyl radical in aerobic condition; otherwise, radical cations usually do not show reactivity towards oxygen O_2. Our results suggest that both mechanisms are operative in MG sensitized oxidation of DETU (Rábai et al., 1993).



An electron transfer from this substrate to the dye results in the formation of leuco base.

HPLC analysis of bleached dye sample

HPLC was carried out to verify the decoloration of dye, whether the bleaching of dye owed to leuco dye formation or degradation may also occur in the reaction mixture. HPLC chromatogram showed the degraded dye solution after 30 min of photolytic treatment of dye. From Figures 3 to 7, it is clear that no absorption peak of dye was observed in chromatogram which indicates that dye is degraded also with the formation of leuco dye. Hence, color loss was due to the degradation of the dye with the reduction as chromatogram showed the small peaks in UV region. It was found out that the dye molecule, decomposed into smaller fragments which conformed that color loss was also related to the degradation along with the reduction, as observed earlier by Ahmed et al. (2010).



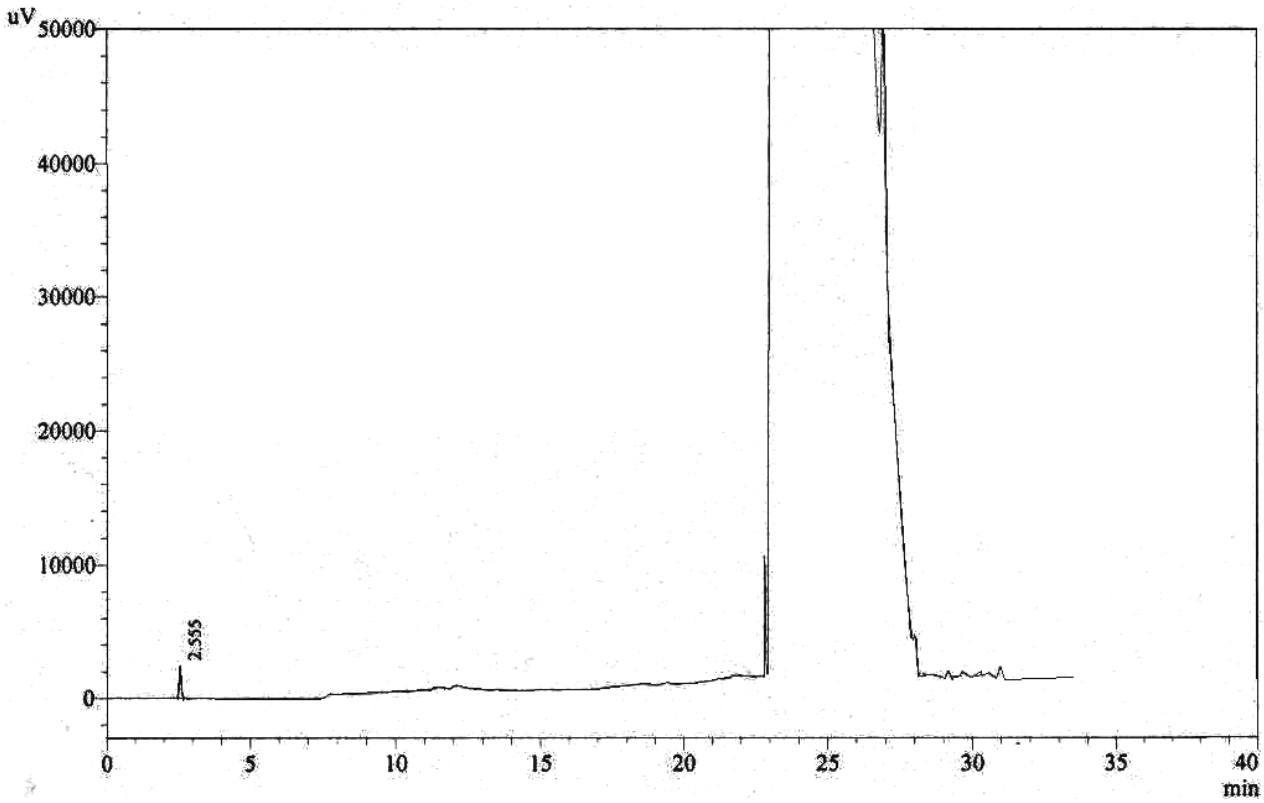


Figure 3. HPLC chromatogram for blank in gradient with 100% methanol and water.

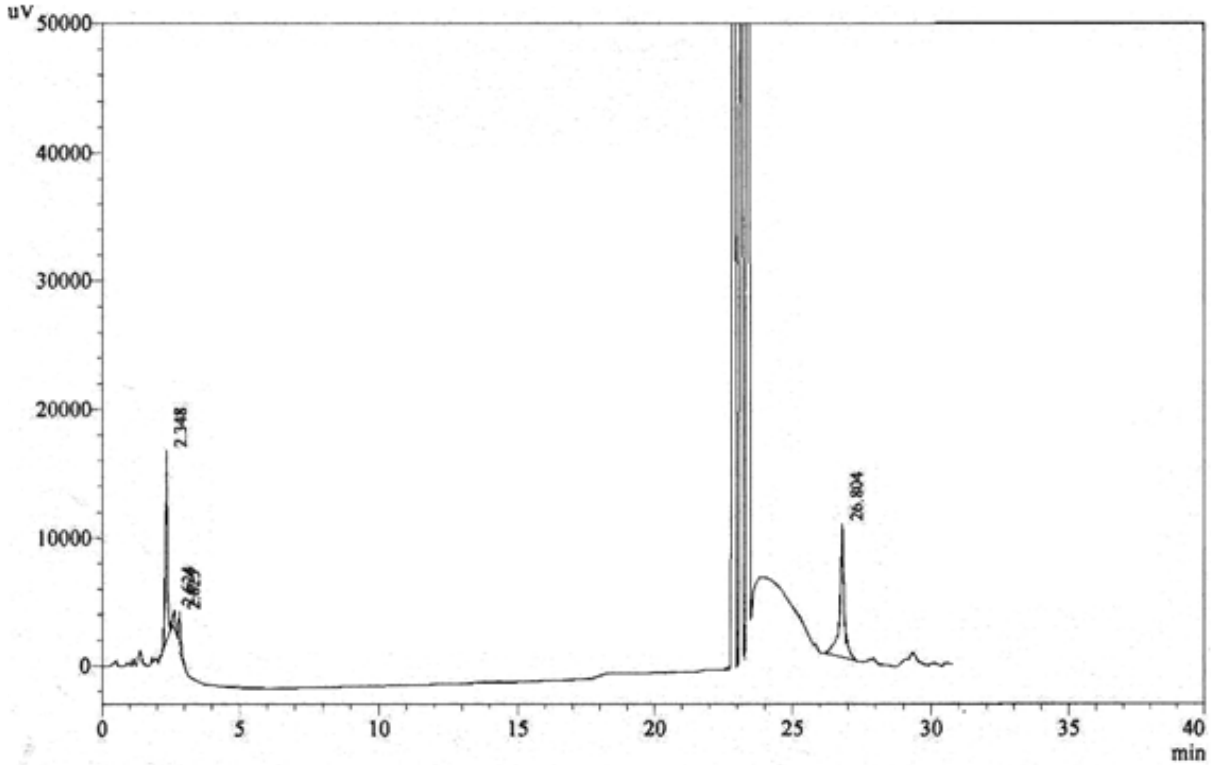


Figure 4. HPLC chromatogram of leuco-MG without medium.

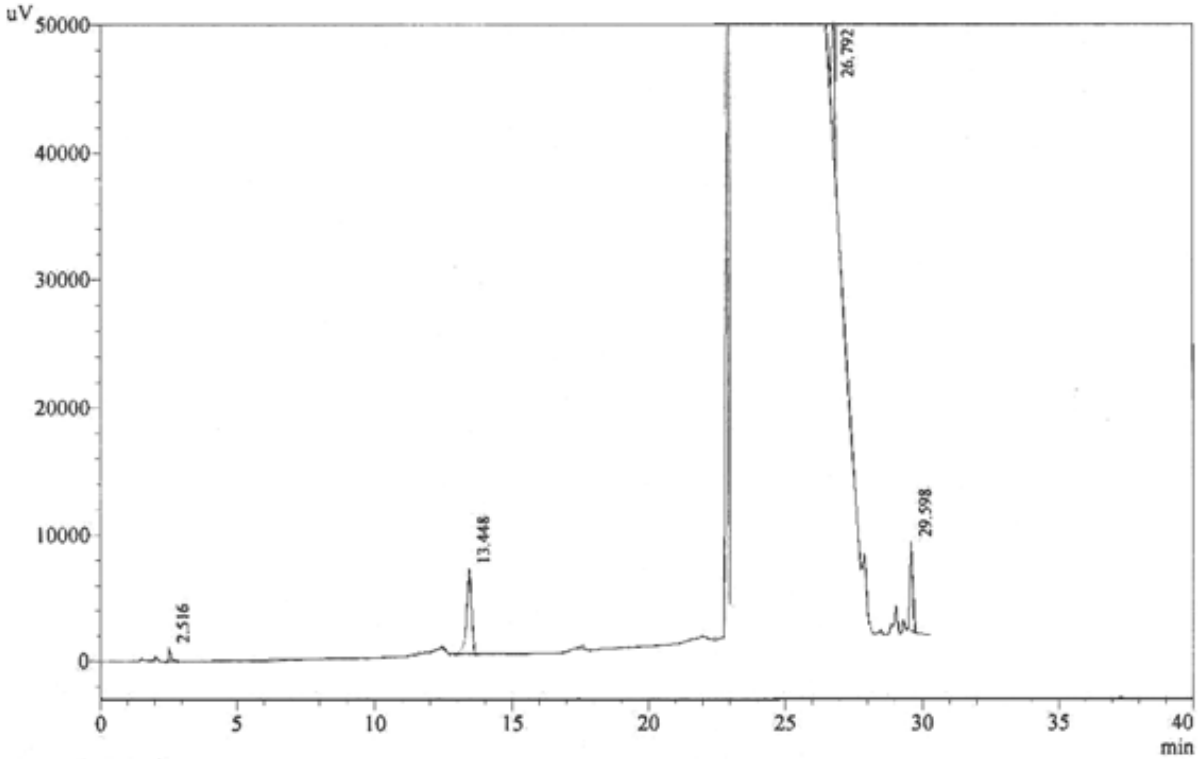


Figure 5. HPLC chromatogram of leuco-MG in the presence of H_2SO_4 medium.

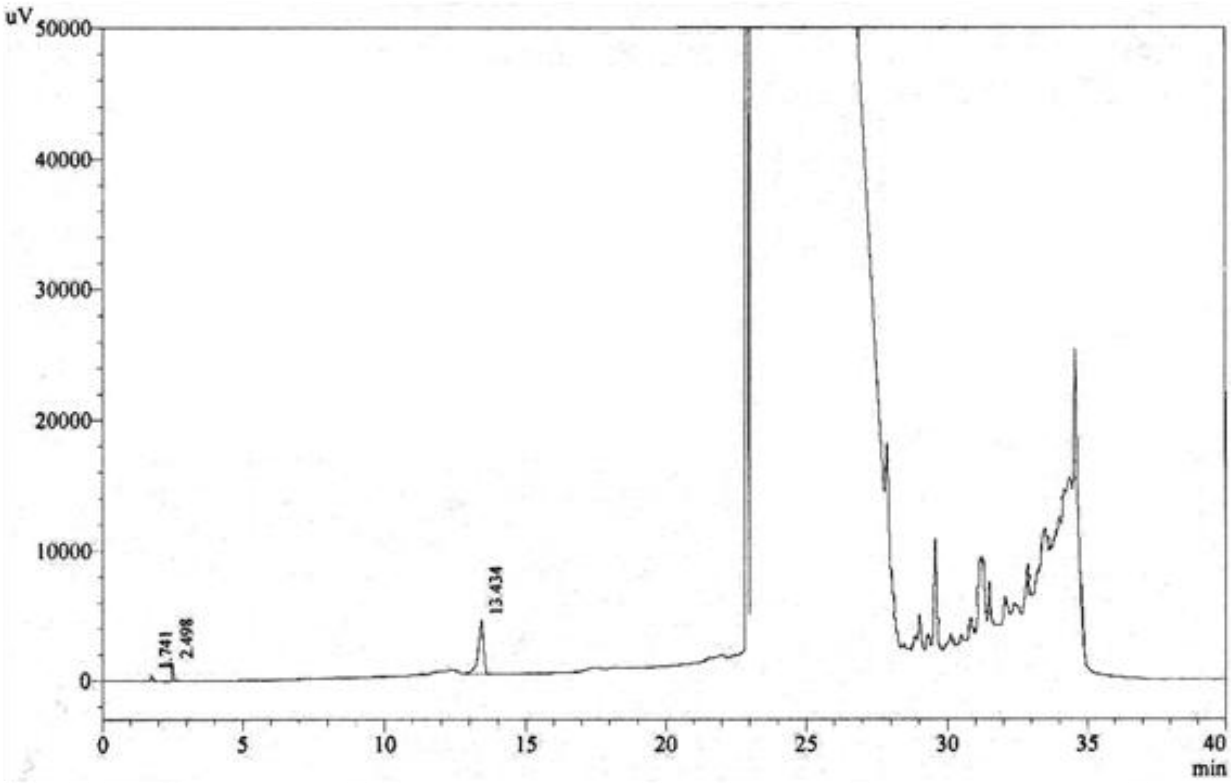


Figure 6. HPLC chromatogram of leuco-MG in the presence of HCl medium.

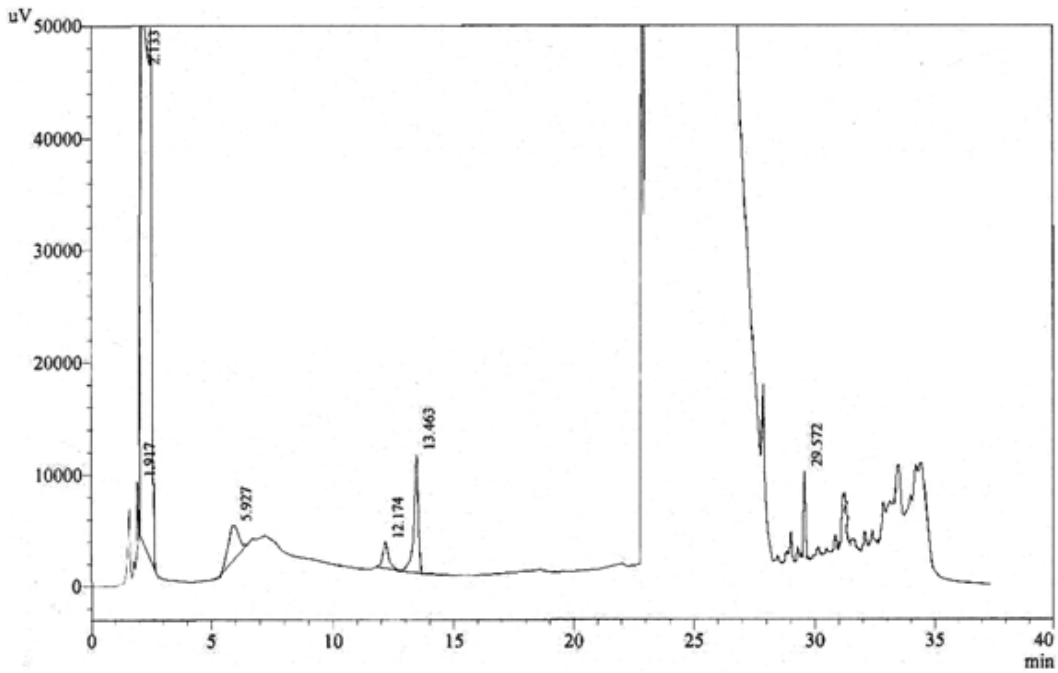


Figure 7. HPLC chromatogram of leuco-MG in the presence of NaOH medium.

Table 4. Effect of change in temperature on rate constant in monoprotic and diprotic acid.

Temperature (K)	HCl		Comparison with literature	H_2SO_4		Comparison with literature
	$v \times 10^5$ (mol.dm^{-3}. s^{-1})	$k \times 10^5$ (s^{-1})	$k \times 10^4$ (s^{-1})	$v \times 10^5$ (mol.dm^{-3}.s^{-1})	$k \times 10^5$ (s^{-1})	$k \times 10^4$ (s^{-1})
293	3	5		7	10	
298	1	2		6	10	
308	1	2	---	8	10	7.14
318	0.2	0.3		3	6	
323	0.5	0.9	15.4	2	3	16.7

Table 5. Activation parameters of the degradation of dye in the presence of HCl.

Temperature (K)	E_a (kJ/mol)	ΔH (kJ/mol)	$-\Delta S$ (J/mol.K)	ΔG (kJ/mol)
HCl				
293		-56.79	514.39	93.93
298		-56.83	514.53	96.50
308	-54.35	-56.91	514.80	101.65
318		-56.99	515.07	106.80
323		-57.04	515.20	109.34
H_2SO_4				
293		-30.09	414.10	91.24
298		-30.13	414.24	93.31
308	-27.65	-30.21	414.51	97.46
318		-30.30	414.78	101.60
323		-30.34	414.91	103.68

Reaction mechanism

$$MG + h\nu \longrightarrow MG^* \quad (3)$$

$$MG^* \xrightarrow{k_1} MG + h\nu \quad (4)$$

$$MG_S^* \longrightarrow MG_T^* \quad (5)$$

$$MG_T^* + O_2 \longrightarrow MG + O_2^* \quad (6)$$

$$MG^* + ASH_2 \longrightarrow AS^* + MGH \quad (7)$$

$$\frac{-d}{dt}[MG] = k_2[ASH_2^*][MG] \quad (8)$$

at steady state,

$$\frac{-d}{dt}[MG] = \frac{k_1 k_2[ASH_2^*][MG]}{k_{-1} + k_2[MG]} \quad (9)$$

The above equations showed the influence of concentration of MG on rate of reaction which is inhibited after addition of dye on reaction mixture. It is therefore evident that equation predicts a zero order to MG which has been actually observed during the rate of reaction. At larger MG, it seems that cationic dye-oxidants solvated and $\Delta S^{\neq}$ decline due to electrons friction.

Conclusion

It was concluded that reduction of methylene green with DETU is based on proton abstraction in acidic medium from reductant. HPLC analysis of reaction mixture showed that dye degradated with the leuco formation through oxidation which results in the fragmentation of reductant DETU.

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