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GC-Mass Spectrokinetics Study of Probable Mechanism of the Oxidation of Diethylthiourea with Toluidine Blue

*M. Qadri, F. Uddin and R. Azmat
Photochemistry Research Lab, Department of Chemistry, University of Karachi, Pakistan
E-mail: *masoodaq @uok.edu.pk

ABSTRACT
Thecurrent study describes the interactive role of diethylthiourea on the bleaching of toluidine blue (tolonium chloride) (TB^+) in acidic and basic media using the GC Mass Chromatography and Spectrophotometric technique. GC-Mass Spectrophotometric analysis 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. The dye redox reaction process followed first order kinetics with respect to TB, DETU showed first order mechanism, first order kinetics with respect to H^+. Enhanced decoloration in the presence of DETU proved that reductant's role is pivotal in the redox reaction. Slow decoloration in basic medium with ions was seen compared to acidic media, suggesting that pH of the medium is significant in the oxidation of DETU. The bleaching reaction of dye was investigated at different temperatures. At pH of 1.0 and 25^0C, the order of reaction is found to be second having rate constant value of 15.81 $mol^{-1}.L\ s^{-1}$,and rate law is suggested to be $-d/dt\ [TBH\ ] = k_2\ [TB^+\ H^+][DETU]$.Different reaction energy parameters were evaluated for a TB^+-DETU reaction, including the energy of activation (E_a = 60.786 $kJmol^{-1}$ (basic medium), 1.669$kJmol^{-1}$ (acidic medium)), enthalpy of activation ($\Delta H^{\neq}$ = -58.267 kJ mol^{-1}(basic medium), -12.6kJ mol^{-1}(acidic medium)), entropy of activation ($\Delta S^{\neq}$ = -131.525$Jmol^{-1}K^{-1}$(basic medium),-243 $Jmol^{-1}K^{-1}$(acidic medium)),and free energy of activation ($\Delta G^{\neq}$ = -98.119$kJmol^{-1}$ (basic medium) and -86.55$kJmol^{-1}$ (acidic medium). A mechanism of interaction of involved ions in dye bleaching and a mechanism of oxidation based on the above findings is proposed.

Keywords: TB, DETU, bleaching of the dye, redox reaction, activation energy.

1. INTRODUCTION

Oxidation of diethylethiourea with TB gave a new aspect, as the oxidant is widely used in the industry as stabilizer[1-4]. GC-mass analysis proved that color of the dyes diminishes with the degradation. Consequently leuco formation of the dye occur in the reaction mixture, these reactions exclusively occurring in textile dye disposable waste material and were neglected and ignored in past. This research described the continuous redox reaction in between dye and diethylthiourea, its degradation and oxidation into smaller fragments which were not reported yet in the highly contaminated presenceof acidic and basic medium which provides a maximum interaction of these species in the industrial drainage streams. Experiments were performed to gain the knowledge of useful and harmful reaction occurring in textile waste water through kinetics technique.

DETU is a very significant derivative of the urea family. It is widely used in paper and leather industries. One cannot ignore the role of the reductants after dying process in open atmosphere in presence and absence of natural solar light.

2. MATERIALS AND METHODS

The experiments are performed according to the sequence: (i) preparation of solutions, (ii) Spectrokinetic measurements, (iii) data analysis (iv) spectral analysis.

2.1 *Preparation of solutions*

Stock solution of toluidine blue (TB^+) = $1.0 \times 10^{-4}$$molL^{-1,}$ Stock solutions diethylethiourea = 0.5 $molL^{-1}$, HCl = 0.5 $molL^{-1}$, NaOH = 0.50 $molL^{-1}$, and NaCl = 0.60 $molL^{-1}$ in 250 mL were prepared in deionized water. Necessary dilutions were made at the time of kinetics measurements

2.2 *Kinetic measurements*

Initially, each kinetic run was made by keeping one reactant varied and the others taken as constant. Mechanism was measured by noticing the absorbance of a mixture of solutions w.r.t. time at each regular 60 s intervals up to 10 min, thermostatistically[5-6]. The absorption spectrum of TB was scanned for absorption maximum peak at a wavelength of 625 nm.

2.3 *Data analysis*

The plot of absorbance vs time gives rate of reaction. The plot of ln Abs. vs time gives the apparent rate constant and the values of the slopes gave its values. The values of the slopes from the plot of ln $(A_o\text{-}A\infty/A_t\text{-}A\infty)$ gave the value of specific rate constant.

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3. RESULTS AND DISCUSSION

GC mass spectrophotometry of reaction mixture was performed in order to confirm the oxidation of the DETU with TB. It was found that molecular ion peak at m/z 132 indicates that the dye decoloration takes place with the degradation of dye that may be attributed with the dissociation of dye complex formed, with DETU present in the reaction mixture, Figure (1,2,3) illustrate these facts.

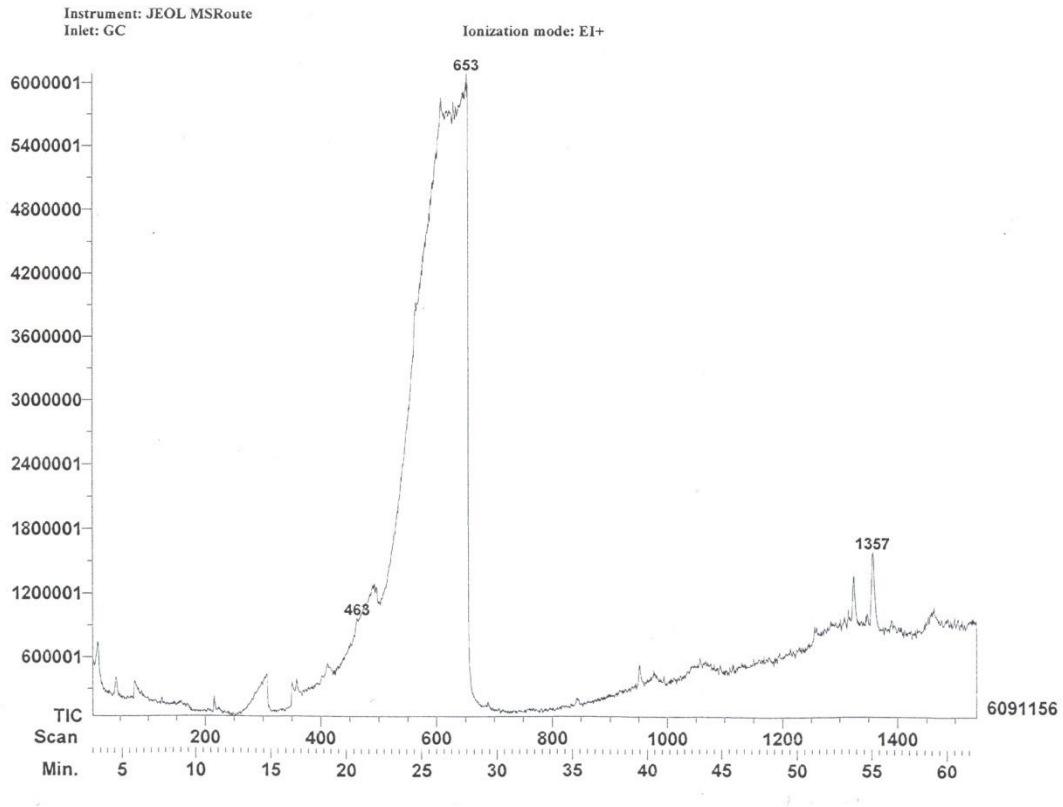


Fig-1: Ionization mode EI+

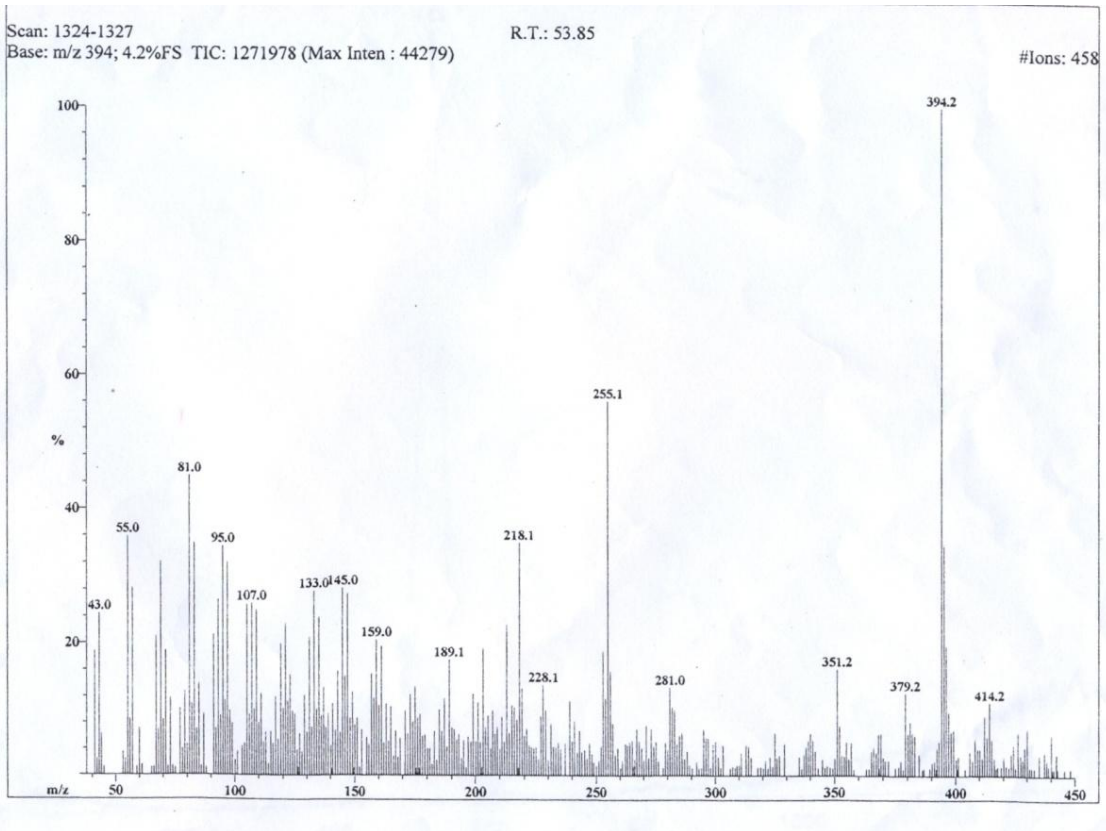


Fig-2: Scan: 1324-1327, Base: m/z 394; 4.2% FS, TIC: 1271978 (Max Inten: 44279), R.T: 53.85

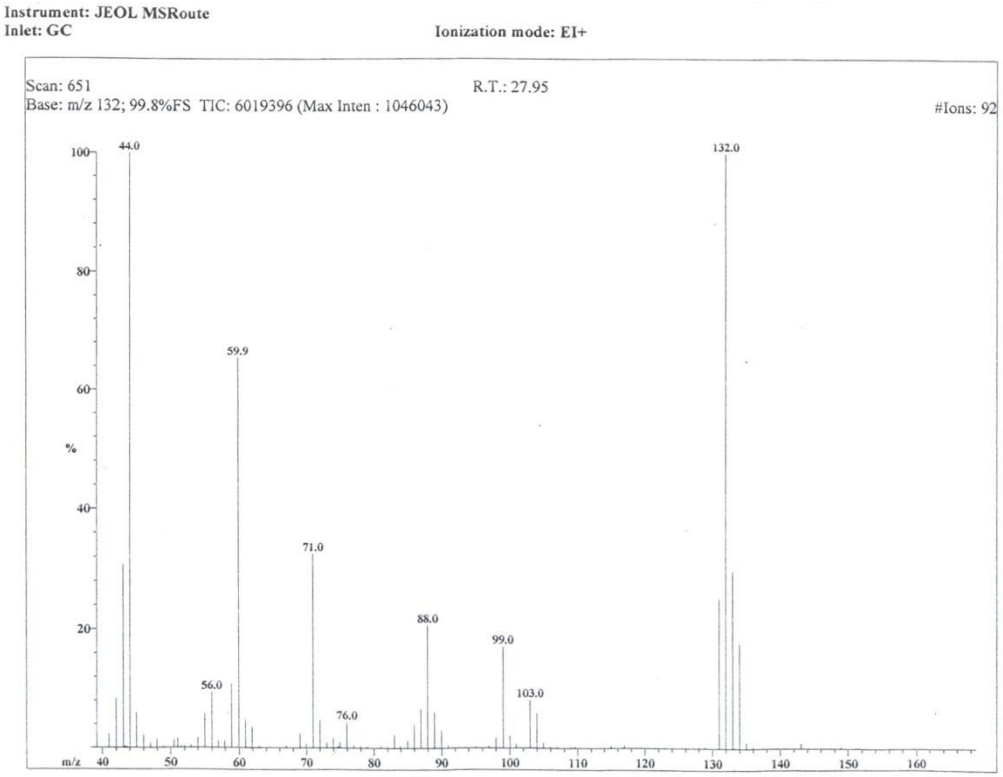


Fig-3: Scan: 651, Base: m/z 132; 99.8% FS, TIC: 6019396 (Max Inten: 1046043, R.T: 27.95)

The DETU oxidation with Toluidine blue was studied at various pH with. The initial rate and the extent of decoloration are reported in Tables (1,2,3,4,5,6) and represented plots are given in the Figures (4,5,6,7,8,9,10,11,12). The absorbance have linear dependence upon time and the slope of the line is equal to the rate constant for different initial concentrations of TB, DETU, H^+ and OH^- ion.

Table-1: Effect of concentration of TB on rate of reaction in aqueous medium

[TB]x10^{5}mol.L^{-1}	**dx/dt x10^{4}mol.L^{-1}s^{-1}**	**K_{obs}s^{-1}x10^4**	**%decoloration**
1.00	0.1	0.50	0.1
2.00	0.4	0.54	0.15
3.00	0.6	0.60	0.3
4.00	0.6	0.67	0.3
5.00	0.6	0.70	0.3

Temperature = 298K, [DETU] = 1.0×10^{-2}mol·dm^{-3}

Table-2: Effect of concentration of TB on rate of reaction in acidic medium

[TB]x10^{5}mol.L^{-1}	**dx/dtmol.L^{-1}s^{-1}**	**K_{obs}s^{-1}**	**%decoloration**
1.00	2.00	11.1	90.05
2.00	4.00	15.0	90.05
3.00	3.00	31.2	97.0
4.00	4.00	32.1	98.02
5.00	3.00	29.0	96.63

Temperature = 298K, [DETU] = 1.0×10^{-2}mol·dm^{-3}, [H^+] = 1.2 mol·dm^{-3}

Table-3: Effect of concentration of DETU on rate of reaction in aqueous medium

[DETU]mol.L^{-1}	**dx/dtx10^{4}mol.L^{-1}s^{-1}**	**K_{obs}s^{-1}x10^4**	**%decoloration**
0.003	0.40	0.10	0.10
0.005	0.45	0.25	0.11
0.01	0.50	0.35	0.15
0.02	0.55	0.60	0.20
0.03	0.60	0.80	0.30

Temperature = 298K, [TB] = $2.0 \times 10^{\square 5}$ mol·L^{-1}

Table-4: Effect of concentration of DETU on rate of reaction in acidic medium

[DETU]mol.L^{-1}	dx/dtmol.L^{-1}s^{-1}	K_{obs}s^{-1}	%decoloration
0.003	4.0	0.03	33.47
0.005	7.0	0.07	61.10
0.01	10.0	0.15	90.63
0.02	11.0	0.31	98.88
0.03	18.0	0.45	99.0

Temperature = 298K, [TB] = 2.0 × 10^{-5} mol·L^{-1}, [H$^+$] = 1.2 mol·dm^{-3}

Table-5: Effect of concentration of H^+ on rate of reaction

[H$^+$]mol.L^{-1}	dx/dtmol.L^{-1}s^{-1}	K_{obs}s^{-1}	%decoloration
0.001	0.06	0.05	0.24
0.01	0.05	0.05	0.24
0.1	2.0	2.0	30.0
0.5	10.1	13.1	67.6
1.0	10.2	15.3	90.5

Temperature = 298K, [TB] = 2.0 × 10^{-5}mol·dm^{-3}, [DETU] = 1.0 × 10^{-2}mol·dm^{-3}

Table-6: Effect of concentration of OH^- on rate of reaction

[OH$^-$]x10^{2}mol.L^{-1}	dx/dtmol.L^{-1}s^{-1}	K_{obs}s^{-1}	%decoloration
0.6	0.2	0.4	6.43
0.9	0.2	0.5	8.62
1.0	2.0	4.0	9.00
3.0	1.0	0.4	8.12
6.0	0.2	0.4	8.00

Temperature = 298K, [TB] = 2.0 × 10^{-5}mol·dm^{-3}, [DETU] = 1.0 × 10^{-2}mol·dm^{-3}

3.1 E*ffect of varied concentration of reductant on TB decoloration*

Kinetics of the DETU oxidation were measured by varying the concentrations of DETU keeping all other variables constant[7-12].

A plot of k verses DETU concentration in presence of acidic or basic medium showed immense effect on dye decoloration which reflect that DETU oxidation was dependent upon its concentration Figures (4,5). A plot of k vs DETU concentration was presented in the Figures (4, 5) in which proved that dye decoloration was enhanced by the presence of reductant and order of reaction was first order in acidic medium and basic medium, the the value of R^2 is (0.99) in acidic medium and (0.95) in basic medium respectively, which predicts high dependency on reaction. At pH of 1.0 and 25^{0}C, the order of reaction is found to be second having rate constant value of 15.81 mol^{-1}.L s^{-1}, and at pH of 9.0, rate constant value of 0.002 mol^{-1}.L s^{-1}.

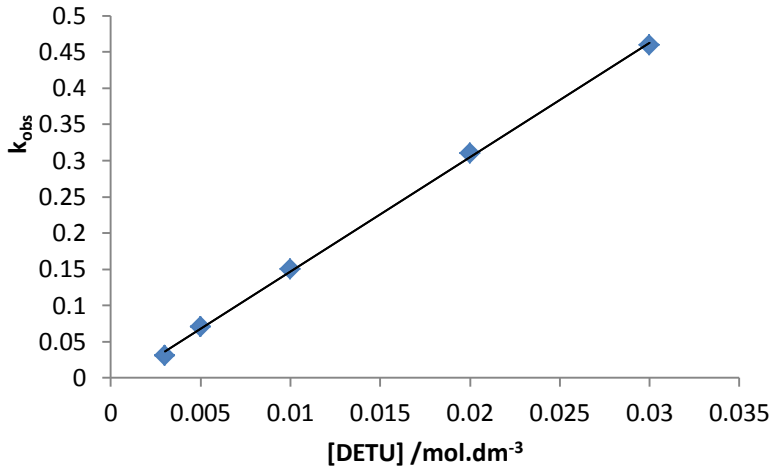


Fig-4: The plot of k vs [DETU] in acidic medium

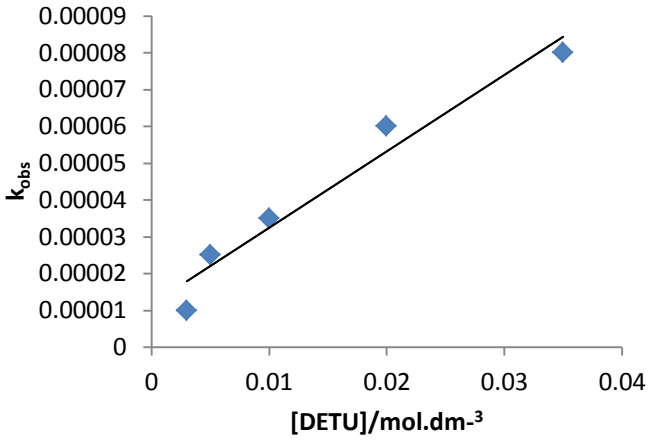
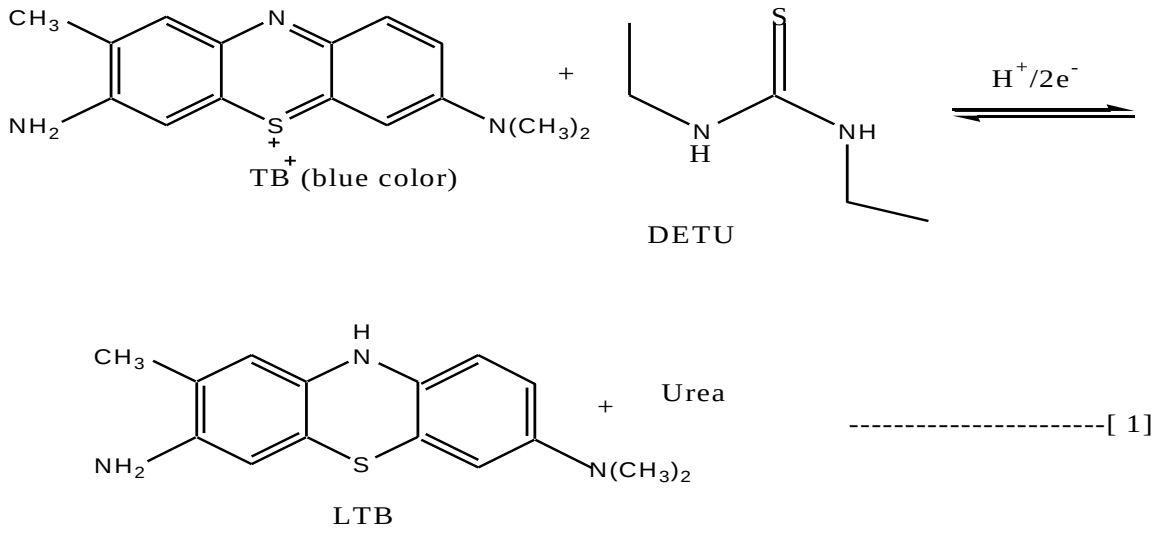


Fig-5: The plot of k vs [DETU] in basic medium.

It also reflects high dependency of DETU on its oxidation, as shown in equation (1).



The TB absorbs photons of light[13-14] and gets in excited state

$$TB^{+} + photons \xrightarrow{k_1} TB^{®} \text{ (excited state)}$$

$$TB^{+} + H^{+} + DETU \xrightarrow{k_2} \text{TBH}$$

$$C_2H_5N\,H(HNC_2H_5)C = S \xrightarrow{k_3} C_2H_5N\,(NC_2H_5)C = O$$

Rate of formation of TB ® (photo excited form) is according to equation

$$\mathbf{r[TB®] = k_1\,[TB]} \qquad (1)$$

Rate of reduction of TB into TBH is according to equation

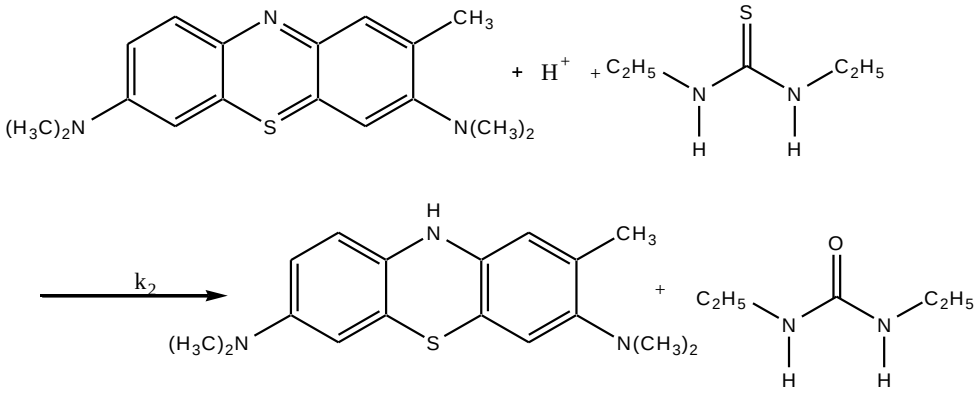
$$\mathbf{r\,[TBH] = k_2\,[TB][H][DTEU]} \qquad (2)$$

Rate of oxidation of DETU is according to equation

$$\mathbf{-\,r[DETU] = k_3\,[complex]} \qquad (3)$$

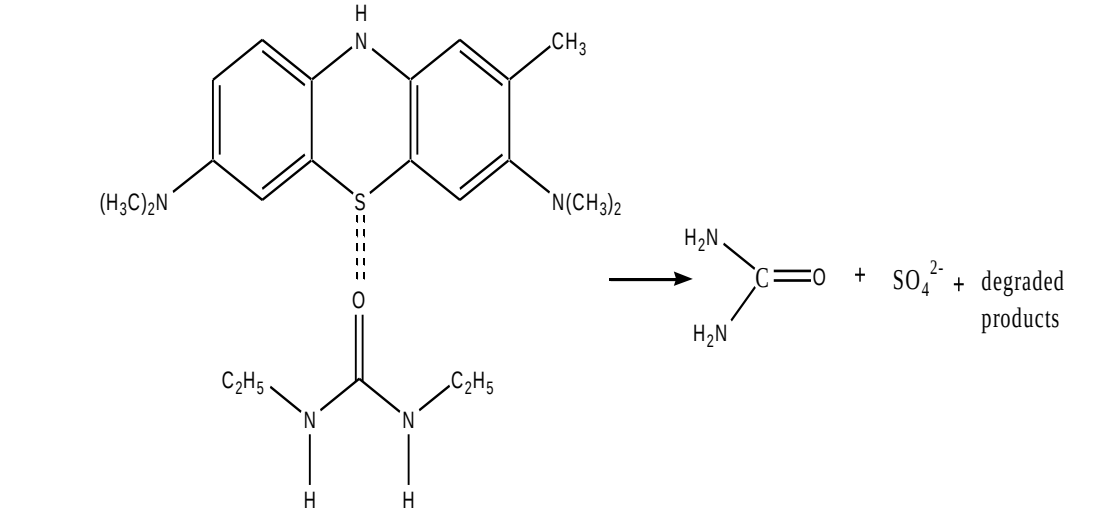
$$\mathbf{r\,[TBH^{+}] = k_1\,[TB®] + k_2\,[TB\,[H^{+}]\,[DETU] = k_3\,[complex]}$$

$$\mathbf{k_1\,[TB] + k_2\,[TBH]\,[H^{+}] - k_3\,[\,complex\,] = 0}$$



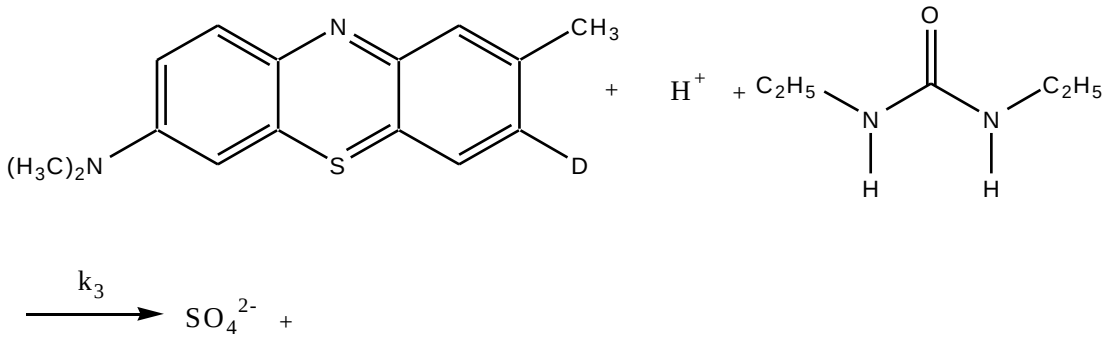
Decoloration

The scan of GC chromatogram of peak yield peaks at 394.2 m/z which proves the reduction of TB in acidic medium.



Complexation

degradation



The above reaction was proved by GC mass chromatographic analysis. Scan of 651 peak showed highest peak at 132.0, which proved dye degradation during reduction process. Eventually it leads to complex formation in the intermediate step as given above.

The second order rate constant value k_2 is 2.0×10^{-2} $mol^{-1}.dm^3s^{-1}$ in aqueous medium and k_1 is 15.81 $mol^{-1}.dm^3$ s^{-1} in acidic medium.

3.2 *Effect of dye, TB concentration on oxidation of detu*

Effect of varied concentration of TB in presence of DETU were reported in the Table (3) and Figures (6, 7, 8), showed that increasing concentration of dye effect significantly and decoloration was found to increase but at higher concentrations of dye the effect got diminished which may be attributed with that at higher concentration of dye, excitation of dye was suppressed or more photon of light was required for large number of molecules in the reaction[4].

The rate constant data was obtained for varied initial concentrations of TB with fixed concentrations of HCl, NaOH and the reductant, Table (3) and respective graphs are shown in Figures (6, 7, 8).

First order trend of TB with DETU in acidic and basic medium, clearly shows that the dye sparks a significant role in the reaction mechanism as shown in equation 2.

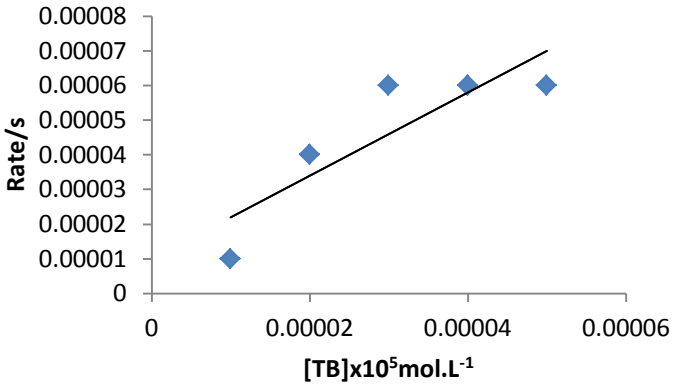


Fig-6: The plot of Rate vs [TB] with DETU in aqueous medium

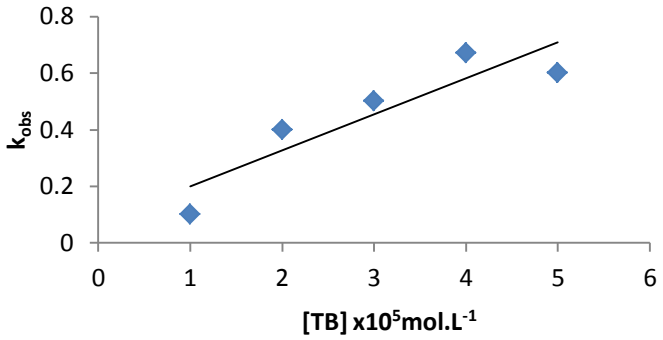


Fig-7: The plot of k_{obs} vs [TB] with DETU in aqueous medium

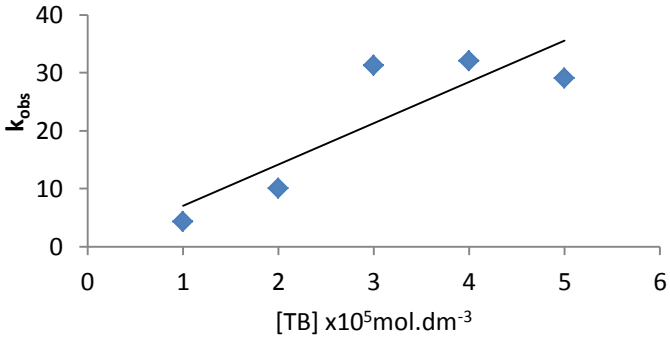


Fig-8: The plot of k_{obs} vs [TB] with DETU in acidic medium

A plot of k_{obs} vs conc. of TB in presence of DETU in aqueous and acidic mediums presented in the Figures (7,8) in which linear regression analysis proved that dye reduction was dependent of the concentration of dye and order of reaction was first order and the values of R^2 shows dependency of reduction on dye concentration.

5.4 *Effect of varied concentration of different mediums on the reduction of TB*

The pH of the reaction mixture was varied by changing the concentration of hydrochloric acid and sodium hydroxide. In acidic medium and in low conc. of dye the reaction fellows pseudo first order mechanism indicating first order dependence with respect to the H^+ ion in HCl, DETU and dye, as shown in Figure (9). The plot of k vs $[H^+]$ shown in

Figure (10) reflect first order dependence with respect to acidic medium. The plots of log dependence of H^+ and OH^- ions presented in the Figures (9, 11) indicate first order kinetics.

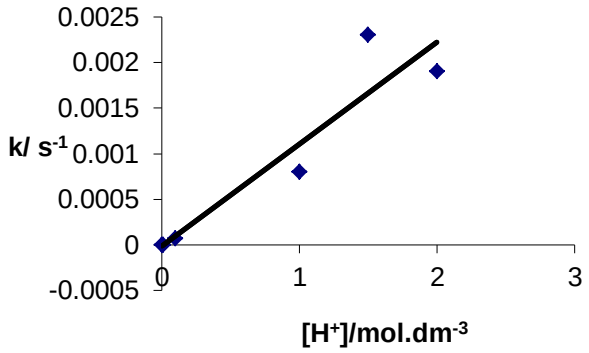


Fig-9: The plot of k vs H^+(HCl) for reaction of TB vs DETU

Whereas in the presence of base, the insignificant value of $R^2 = 0.329$ shows, the less dependence of rate of reduction in case of DETU to the concentration of OH^- ions, as shown by Figure (12, 13).

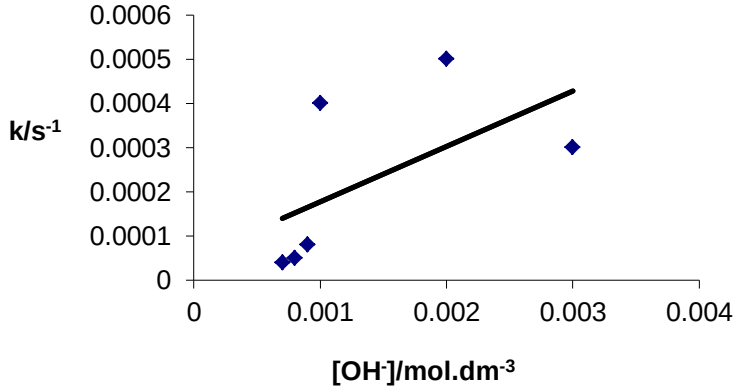


Fig-10: The plot of lnk vs ln[NaOH] for reaction of TB vs DETU

5.5 E*ffect of temperature on the reduction of* TB

Temperature plays an effective role in dye decoloration process, which increases with an increase in temperature. Dye reduction with DETU was studied at elevated temperatures between 303 - 343 K at low and high pH. The plots of lnk vs 1/T were linear as shown in Figure (11, 12). It was found that the rate of reaction was low at low temperature but significantly increased with an increase in temperature. Thermodynamic activation parameters were computed and are reported in the Table (5).The energy of activation for the oxidation of DETU is (E_a = 1.669 kJ·mol^{-1}) in acidic medium and for DETU is (E_a = 60.786 kJ·mol^{-1}) in basic medium.

The negative values of $\Delta H^{\neq}$, ($\Delta H^{\neq}$ = -12.6 kJ·mol^{-1}) in acidic medium and ($\Delta H^{\neq}$ = -58.2 kJ·mol^{-1}) in basic medium showed that enthalpy is the driving force in the formation of the complex, and negative values of entropy ($\Delta S^{\neq}$ = -131.525Jmol^{-1}K^{-1}(basic medium),-243 Jmol^{-1}K^{-1}(acidic medium) shows that entropy is also responsible for the formation of the complex which involves one charged species and solvent molecule for the decoloration of dye. For DETU the negative values of $\Delta G^{\neq}$, ($\Delta G^{\neq}$ = -86.55kJ·mol^{-1} in acidic medium and $\Delta G^{\neq}$ = -98.11 kJ·mol^{-1} in basic medium indicates that the reaction is spontaneous under normal conditions but enhanced by different thermodynamic and chemical parameters[15-17].

Table-5: Effect of Temperature on rate of reaction of TB Vs DETU in Acidic medium([HCl]=1.2 mol.L^{-1}),TB] = 2.0 × 10^{-5}mol·dm^{-3}, [DETU] = 1.0 × 10^{-2}mol·dm^{-3}

Temperature (K)	10^4 (dx/dt) (mol.dm^{-3}.s^{-1})	10^4 k_{obs} (s^{-1})	% decoloration
303	10.0	29.0	96.63
313	11.0	31.0	79.65
323	11.0	41.0	92.38
333	13.0	50.0	92.00
343	15.0	55.0	99.65

Table-6: Effect of Temperature on rate of reaction of TB Vs DETU in basic medium ([NaOH] =1x10^{-2} mol.L^{-1}),[TB] = 2.0 × 10^{-5}mol·dm^{-3}, [DETU] = 1.0 × 10^{-2}mol·dm^{-3}

Temperature (K)	10^4 (dx/dt) (mol.dm^{-3}.s^{-1})	10^4 k_{obs} (s^{-1})	% Decoloration
303	0.2	0.5	6.85
313	0.3	0.7	7.17
323	0.5	0.9	11.76
333	1.0	2.0	12.50
343	2.0	3.0	15.70

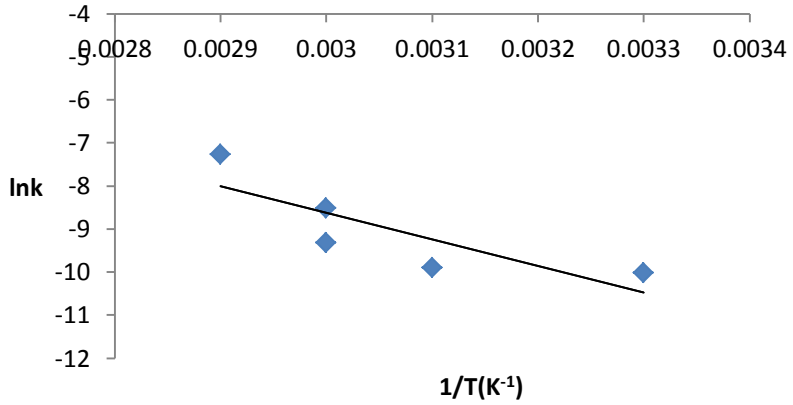


Fig-11: A plot of ln k with 1/T for the reaction of DETU with NaOH

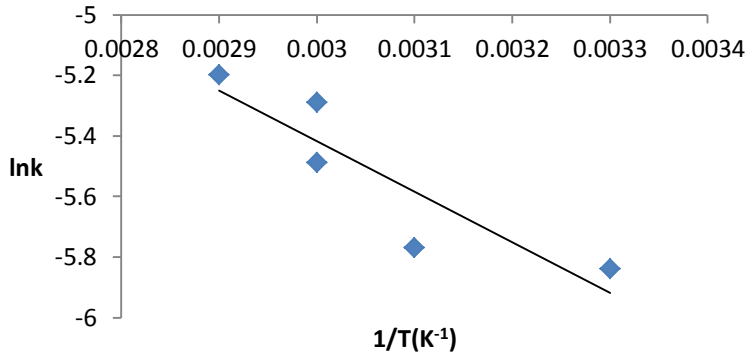


Fig-12: A plot of ln k with 1/T for the reaction of DETU with HCl

From the above graphs it clearly concludes that the rate of reaction was affected by the change in temperature.

6. CONCLUSIONS

The oxidation reaction of DETU with TB was carried out in alkaline and acidic media and temperature variations to predict the of mechanism spectrophotometrically. It was observed that the oxidation reaction was tremendously fast in acidic medium and followed pseudo first order kinetics. Industrial drainage contain mostly organic, inorganic compounds and dyes which remain non degradable and creates toxicity in the effluents. These chemicals often react with each other and form more complex compounds which add to this lethal scenario. We have focused on the possible reactions and the type of interactions that can occur in these circumstances.

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