



## Photoinduced electron transfer reaction of 2-mercaptothiazoline and methylene blue: Mechanism and kinetics

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### ABSTRACT

2-Mercaptothiazoline (2MT) is a more toxic as compare to the thiazole and the photosensitized reaction of 2MT with methylene blue (MB) in the alkaline medium using visible light has been studied to convert 2MT to less toxic thiazole. 2MT shows the  $\lambda_{max}$  at 270 nm between the pH range 2 – 6 and the  $\lambda_{max}$  at 235 nm in the pH range 8 – 12. The irradiation of MB molecule with visible light excites it to singlet excited state which gives triplet excited state on ISC which interacts with 2MT anion and transfer its energy to 2MT anion and comes back to ground state (dipole-dipole energy transfer mechanism). The triplet excited state of 2MT anion gives thiazole radical and sulphur radical anion. The thiazole radical will abstract hydrogen from a hydrogen donor to form thiazole. The sulphur radical anion will react with a proton to form a  $SH^\circ$  radical. As the reaction precedes the thiol form is converted to anion form. The apparent rate of the reaction has been calculated and the effect of pH, concentration of the sensitizer, the light intensity on the apparent rate of the reaction has been studied. The quantum efficiency of the photochemical reaction is calculated using potassium ferri oxalate actinometer and the effect of the concentration of the substrate on the quantum efficiency is calculated. The reaction mechanism and the excited states involved have been suggested.

**Keywords:** 2-Mercaptothiazoline, Photosensitizer reaction, Exciplex formation, Singlet oxygen, Dipole-dipole energy transfer mechanism

### INTRODUCTION

Now a day many toxic organic compounds from different sources are discharged into the water bodies and the problems of water quality have become more important than the quantity of water. How toxic these compounds are in a given environmental system depends on transport and degradation processes. To predict their fate in the natural environment and to assess their risk, it is necessary to improve our knowledge on their chemical reactions under environmental conditions. The classical biological oxidation methods failed to eliminate such micro pollutants to the desired level where as physicochemical technique just transferred them from one phase to another without destroying them. Such classical biological oxidation methods and physicochemical techniques are useful only for the high level concentrations of pollutants, but when the pollutants are present in a very trace level such methods have failed to remove these pollutants from water bodies. Photochemical transformation is one of the main abiotic degradation pathways occurring in natural waters to convert this toxic compound into non-toxic material [1, 2] at a very trace level and has received increasing interest in the last three decades. Phototransformation of pollutants may take place through different pathways. Direct photolysis can occur if the considered pollutant absorbs solar light. However, the ability to undergo chemical changes after the absorption of photons is an intrinsic property of the molecule and can vary drastically from one compound to the other. Photoinduced transformations mediated by components of the aquatic environment can also occur. In particular, dissolved natural organic matter (DOM), absorbing a large portion of photons, is a potential photosensitizer. Singlet oxygen, superoxide ion/ hydroperoxyl radicals, hydroxyl radicals

and organic peroxy radicals were proved or proposed to be generated in natural waters under the influence of sunlight.

The structure of 2-Mercaptothiazoline (2MT) is composed of an exocyclic mercapto group and a heterocyclic molecule that contains sulfur, nitrogen and carbon atoms. 2MT has been used as a biocorrosion inhibitor, an antifungal reagent, and a brightening and stabilization agent in many industrial processes [3, 4] hence, it has been frequently detected in both waste water treatment plant and surface water and can come into contact with potable water and can easily enters to food cycle. 2MT is harmful according to its Material Safe Data Sheet and exhibits persistence to microbial degradation. Therefore, 2MT is an aqueous pollutant of concern in water and wastewater systems.

Chen *et al.*[5] investigated decomposition of 2MT via treatment using ozone only. Their results indicated that the heterocyclic structure of 2MT has high resistance to ozone molecules for proceeding with further oxidation. Recently, Chen *et al.* [6] studied the decomposition of 2MT in an aqueous solution by ozonation with UV radiation and reported the complete mineralization of 2MT via O<sub>3</sub>/UV photolysis, accompanied with the generation of sulfate, ammonium and nitrate ions. The energy of incoming solar spectrum, ultraviolet radiation ( $\lambda < 400$  nm) accounts to only less than 4%, while the visible light is more than 50%. Hence, effective utilization of the visible light is an attractive area of photochemical research. The bond dissociation energy per mole for most of the molecules lies between 150 kJ and 600 kJ. These energies are available from Avogadro's number of photons of wavelengths lying between 800 nm and 200 nm respectively, which correspond to the visible and near ultraviolet regions of the electromagnetic spectrum. The same range of energies is required for electronic transitions in most atoms and molecules. Phototransformation of pollutants under natural conditions may be a complex process. In order to understand the mechanisms involved it is necessary to investigate photosensitized transformations under relevant experimental conditions.

In the present work, we focused on the photosensitized reaction of the 2MT in the aqueous alkaline medium on irradiation with visible light. The cationic dye, methylene blue has been used as photosensitizer [7-10]. The kinetics of the photodegradation reaction has been studied. The effects of the pH, the concentration of the sensitizer, the concentration of the substrate and the light intensity have been evaluated on the rate of the reaction. The reaction has been used to determine the quantum efficiency and whether the reaction is monophotonic or biphotonic. The scavenging technique was used to evaluate the role played by free radical and singlet oxygen and to assess the mechanisms involved in the light-induced reactions.

## EXPERIMENTAL SECTION

2MT, Methylene Blue, Potassium trioxalate ferrate, Ammonium ferric sulphate, Sodium Acetate, phenanthroline, were used as received. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were analytical grade. Ethyl alcohol was HPLC grade. All chemicals were used as received. Water was doubly distilled. The solutions were kept in the dark at room temperature and were diluted as per the requirement.

100 W tungsten filament light source has been used for the exposure of the sample solution, convex lens is used to converge the irradiation and a glass water jacket is used to decrease the temperature of the solution. Light intensity is measured using "Light intensity measurement meter" (form Iwiss Solar, Model Number : TM206). All the spectral measurements have been done on UV-Vis spectrophotometer (Chemito – 2100). The pH was adjusted by addition of HCl or NaOH solutions, respectively and has been measured using pH-meter (Systronics, India) with glass calomel electrode.

The four sets of 2MT solution ( $4.0 \times 10^{-5}$  mol L<sup>-1</sup>) in alkaline aqueous medium were prepared. Two of them contain methylene blue (MB) ( $1 \times 10^{-5}$  mol L<sup>-1</sup>) as a photosensitizer. Two flasks, each containing methylene blue (MB) and without MB were kept in dark for 24 hour while remaining similar flasks were exposed to the visible light from 100 W tungsten lamp. The course of the reaction was followed by recording the spectrum of the exposed solution with a control solution in the range of 200-300 nm against reagent blank. The flask kept in the dark and the flask exposed without sensitizer did not show difference in the spectrum when compared to the control; while the exposed flask containing sensitizer showed shift in  $\lambda_{\text{max}}$ .

The effect of varying concentration of MB (in the range of  $4 \times 10^{-6}$  mol L<sup>-1</sup> to  $2 \times 10^{-5}$  mol L<sup>-1</sup>) and 2MT (in the range of  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> to  $5.0 \times 10^{-5}$  mol L<sup>-1</sup>) on the apparent rate of the reaction has been studied respectively. The solutions were deaerated or saturated with O<sub>2</sub> by purging with nitrogen or O<sub>2</sub> respectively, for 30 min via a needle through the cap. The effect of the free radical scavenger on the photo sensitized reaction was studied by changing the medium from aqueous alkaline to methanolic alkaline. Light intensity can be varied by changing the

distance of the sample solution from the tungsten lamp source, and intensity was measured using "Light intensity measurement meter". The study was carried out at room temperature and pressure. The quantum yield of the photo reaction has been evaluated using potassium ferrioxalate actinometer.

## RESULTS AND DISCUSSION

### 1.1 Spectral Characteristics

Experiment shows that the 2MT ( $4 \times 10^{-5} \text{ mol L}^{-1}$ ) exhibits one well-defined maxima one at 270 nm ( molar absorptivity =  $13,667 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) between the pH range 2 – 6 and the maxima at 235 nm (molar absorptivity =  $17,080 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) is observed in the pH range 8 – 12. The band at 270 nm in acidic medium has characteristic of the absorption band of  $\pi \rightarrow \pi^*$  transition, shifts to the shorter wavelength at 235 nm in the alkaline medium and shows increase in the molar absorptivity.

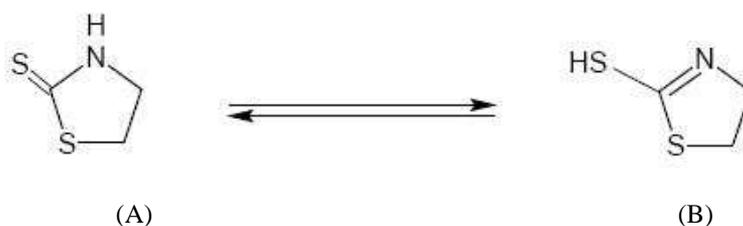


Fig 1 Structure of 2-Mercaptothiazoline

2MT exists as protonated and deprotonated forms in the pH range 2 – 12 which show a marginal change in molar absorptivity with change in the pH of the solution. The protonated form can interact with  $\text{OH}^-$  and forms an anion in the alkaline solution. The spectral changes are reversible depending on the pH of the solution. The molar absorptivity values were plotted against pH and the curve obtained exhibited an inflection at pH 6. Thus it was concluded that below pH 6, 2MT largely exists as a protonated species where as at  $\text{pH} > 6$ , it exists as a deprotonated species.

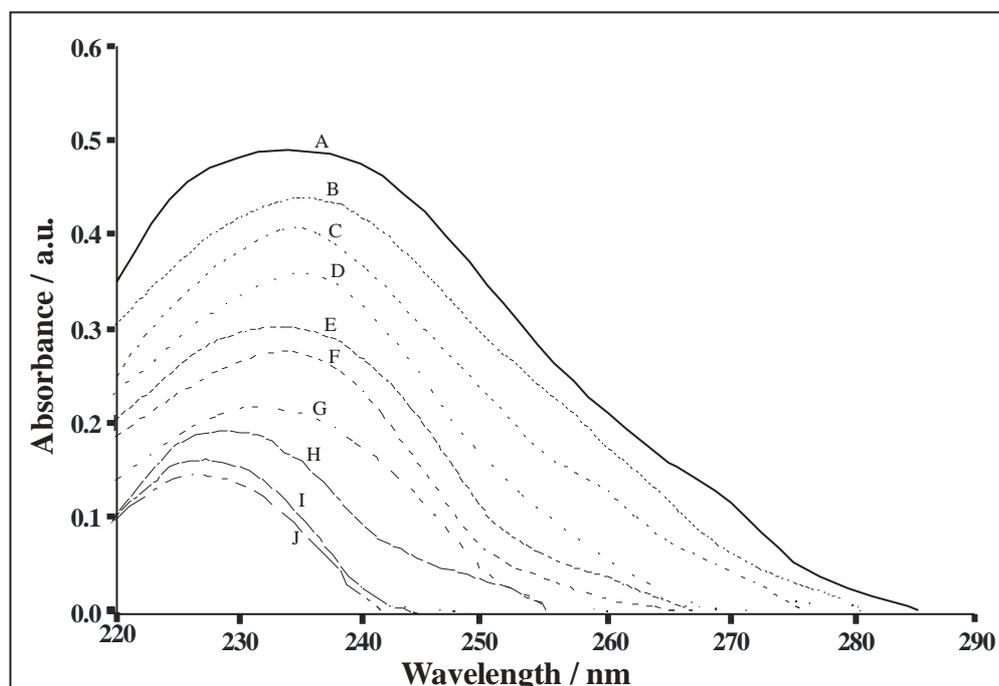


Figure 2 Absorption spectra ((A) at  $T_0$ , (B) at  $T_{10}$ , (C) at  $T_{20}$ , (D) at  $T_{30}$  (E) at  $T_{40}$ , (F) at  $T_{50}$ , (G) at  $T_{60}$ , (H) at  $T_{70}$ , (I) at  $T_{80}$  (J) at  $T_{90}$ ) of the photosensitized reaction of 2MT with MB, 2MT:  $4 \times 10^{-5} \text{ mol L}^{-1}$ , MB:  $1 \times 10^{-5} \text{ mol L}^{-1}$ , time interval: 10 mins, 100 W tungsten lamp, pH 11.

Previous studies have shown the complete mineralization of 2MT via  $\text{O}_3/\text{UV}$  photolysis however in the present study 2MT was found to be photo stable in acidic as well as in the alkaline medium, when irradiated by visible light.

It was also found during the experiment that 2MT and MB don't interact in the ground state but when the reaction mixture containing 2MT ( $4 \times 10^{-5} \text{ mol L}^{-1}$ ) and MB ( $1 \times 10^{-5} \text{ mol L}^{-1}$ ) maintained at different pH between 2 to 12 were exposed to the visible radiation and the spectra were recorded against the reagent blank, the reaction mixture does not show any significant change in the pH range 2 – 6 but it undergoes photoreaction in the pH range of 8 – 12. The changes of the absorption spectrum were plotted against time which show decrease at the  $\lambda_{\text{max}}$  235 nm (Figure 1) and shows increase in the absorbance at 225 nm with time and an isosbestic point was not observed and this indicates that the reaction does not consist just in the transformation of one species to another.

### 1.2 Determination of the Apparent Rate Constant and Effect of Different Parameters on Apparent Rate Constant

The reaction follows the first order reaction kinetics as the plot of  $2 + \log \text{OD}$  (optical density) vs. time (at 235 nm) is a straight line with a positive slope (Figure 3). The rate constant (apparent  $k$  value) has been determined by the expression:

$$\text{Rate constant} = 2.303 \times \text{slope}$$

The half life of the reaction has been observed at different concentration of the substrate and  $t_{1/2}$  value is constant over the above range of the substrate concentration.

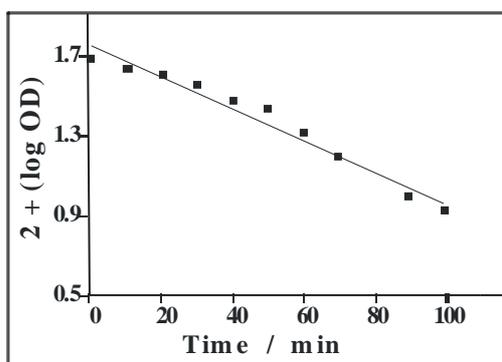


Figure 3 [2 + log OD] Vs Time plot of the photosensitized reaction of 2MT with MB on exposure at 235 nm, 2MT:  $4 \times 10^{-5} \text{ mol L}^{-1}$ , MB:  $1 \times 10^{-5} \text{ mol L}^{-1}$ , time interval: 10 mins, 100 W tungsten lamp, pH 11.

### 2.2.1 Effect of the pH

In this investigation, the effect of the pH value on the 2MT photo degradation with MB in aqueous medium was studied in the pH interval range from 2 to 12. Figure 4 showed the dependence of apparent  $k$  value for 2MT degradation on the pH in the presence of  $1 \times 10^{-5} \text{ mol L}^{-1}$  MB, under  $15 \times 10^8 \text{ E/s}$  visible light intensity. The protonated and deprotonated form do not interact with excited MB molecule directly. 2MT is an electron-pair donor as the Lewis base, and may belong to the polydentate ligand because one 2MT molecule has the electron donor properties of not only N-atoms but also S-atoms [12]. The anion of the protonated form can undergo electron transfer reaction with excited MB molecule which acts as electron acceptor. The pH of the reaction mixture influences both methylene blue and 2MT.

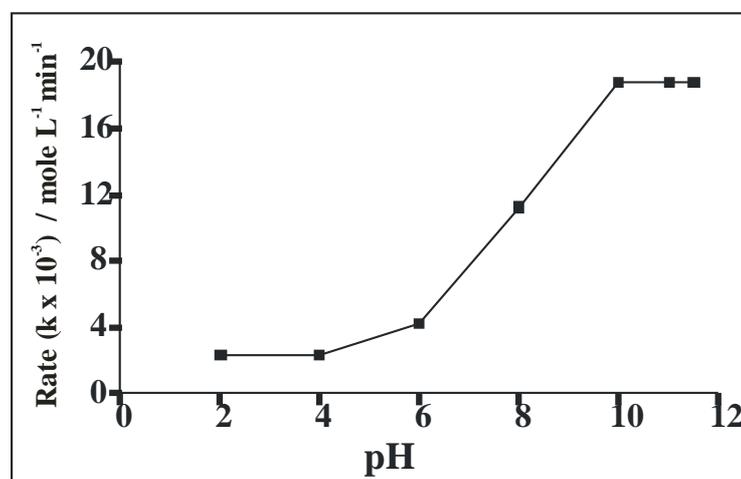


Figure 4 Effect of the pH on the apparent rate of the reaction measured at 235 nm, 2MT:  $4 \times 10^{-5} \text{ mol L}^{-1}$ , MB:  $1 \times 10^{-5} \text{ mol L}^{-1}$ , time interval: 10 mins, 100 W tungsten lamp, pH 11.

### 2.2.2 Effect of the Initial Concentration of Sensitizer

Figure 5 showed the dependence of apparent  $k$  value of the photodegradation of 2MT on the initial concentration of sensitizer under  $15 \times 10^8$  E/s visible light irradiation. The results showed that the photo degradation of 2MT did not occur in the absence of MB. However, 2MT degradation could be efficiently enhanced in the presence of MB. 2MT has its  $\lambda_{\max}$  below 400 nm and is not photodegraded directly by the visible light. Methylene blue absorbs visible radiation at 665 nm and gets excited, which on collision with the 2MT, transfers energy to it. The first-order apparent kinetic constant ( $k$ ) for 2MT degradation increased with increasing sensitizer concentration then becomes constant with increasing sensitizer concentration. However, the first-order kinetic constant for 2MT degradation decreased as the MB concentration reached above a threshold level where the self deactivation of the sensitizer molecule takes place by intermolecular collision [13]. Therefore, the optimal sensitizer concentration value was  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> which mostly favoured the photo degradation of 2MT in the experimental condition.

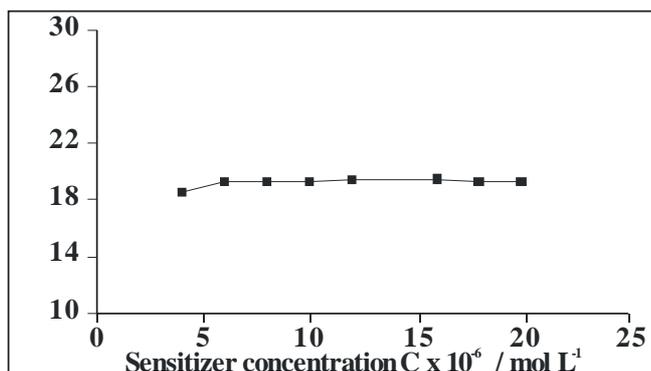


Figure 5 Effect of the sensitizer concentration on the apparent rate of the reaction at 235 nm, 2MT:  $4 \times 10^{-5}$  mol L<sup>-1</sup>, MB:  $4 \times 10^{-6}$  mol L<sup>-1</sup> to  $2 \times 10^{-5}$  mol L<sup>-1</sup>, time interval: 10 mins, 100 W tungsten lamp, pH 11.

### 2.2.3 Effect of the Initial Concentration of Substrate

The first-order apparent kinetic constant  $k$  remains the same  $19.32 \times 10^{-3}$  min<sup>-1</sup> with increasing substrate concentration from  $2 \times 10^{-5}$  mol L<sup>-1</sup> to  $5 \times 10^{-5}$  mol L<sup>-1</sup> and decreases slightly at the higher concentration of substrate. Obviously, there should be an optimal concentration of substrate ( $4 \times 10^{-5}$  mol L<sup>-1</sup>) for 2MT degradation. The first-order apparent kinetic constants  $k$  remaining constant in the concentration range shows that the reaction is independent of the initial concentration of the substrate [14].

### 2.2.4 Study in Aerobic and Anaerobic Conditions to Check a Possible Involvement of Singlet Oxygen

Chen et al reported the complete mineralization of 2MT via ozonation and via O<sub>3</sub>/UV photolysis therefore the reaction was studied in the anaerobic condition to observe the participation of singlet oxygen during the photosensitized reaction. The cationic dye methylene blue – photo sensitizer - absorbs the visible radiation and goes to the singlet excited state and is converted to the triplet state by intersystem crossing (ISC). The excitation energy of the sensitizer molecule is transferred to <sup>3</sup>O<sub>2</sub> molecule and converts it to the singlet state, while photo sensitizer molecule returns to the ground state. This singlet oxygen is a highly reactive species which gives the photo oxygenation reaction. Methylene blue is reportedly efficient sensitizers for the conversion of triplet oxygen to singlet oxygen in the presence of light [15-19]. The first-order apparent kinetic constant was calculated for the exposed solutions of the different concentration of the substrate [2MT] and the sensitizer MB in the aerobic as well as in the anaerobic condition. The first-order apparent kinetic constant in the anaerobic condition  $17.23 \times 10^{-3}$  min<sup>-1</sup> at 235 nm, does not show change and remains the same ( $18.76 \times 10^{-3}$  min<sup>-1</sup> at 235 nm) as in the aerobic condition. The  $\phi$  value of the reaction was also calculated in the anaerobic condition of the reaction which remains constant and same as in the aerobic condition. However the experimental result suggests that the singlet oxygen does not participate in the photosensitized reaction of 2MT.

### 2.2.5 Effect of the Free Radical Scavenger

The effect of the free radical scavenger on the photosensitized reaction of 2MT was studied by changing the medium from aqueous alkaline to methanolic alkaline. The solutions of the different concentration of substrate [2MT] and the sensitizer MB were prepared in the alkaline methanolic solution and irradiated with the visible light. 2MT shows  $\lambda_{\max}$  at 235 nm in the alkaline methanolic solution. The first-order apparent kinetic constant for the 2MT degradation reaction in the aqueous alkaline medium was  $18.87 \times 10^{-3}$  min<sup>-1</sup> at 235 nm changed drastically to  $2.303 \times 10^{-3}$  min<sup>-1</sup> at 235 nm in the alkaline methanolic solvent. The photochemical reaction shows sharp decrease in the alkaline methanolic solvent suggests that there is free radical formation during the reaction [20].

### 2.2.6 Effect of the Light Intensity

Light intensity is another important factor to be considered during photochemical process. Generally, higher light intensity can lead to higher degradation rate for organic pollutants in photochemical reaction. The same results were obtained in this investigation as shown in **Table 1**. The solutions of the different concentration of the substrate [2MT] and the sensitizer MB were prepared in the aqueous alkaline solution and irradiated with the visible light of the different intensity. The increase of the light intensity [Einstein / second (E/s)] shows positive effect and the first-order apparent rate constant of the reaction increases as the light intensity increases. The increase in the number of the photons increases the number of the excited sensitizer molecule and the apparent rate of the reaction also increases. A linear relationship has been observed between the light intensity and the first-order apparent rate constant of the reaction.

**Table 1** Effect of the Light Intensity on the apparent rate of the reaction and on the quantum efficiency at 235 nm, 2MT:  $4 \times 10^{-5}$  mol L<sup>-1</sup>, MB:  $1 \times 10^{-5}$  mol L<sup>-1</sup>, time interval: 10 mins, 100 W tungsten lamp, pH 11

Light Intensity ( $1 \times 10^8$ ) E/s	Rate of the Reaction at 235 nm ( $r \times 10^{-3}$ ) mole / L min [ $r \pm 0.5$ ]	Quantum efficiency
5	6.75	0.50
10	13.42	0.51
15	19.45	0.51
20	24.56	0.51
25	31.45	0.51

### 2.3 The Quantum Efficiency

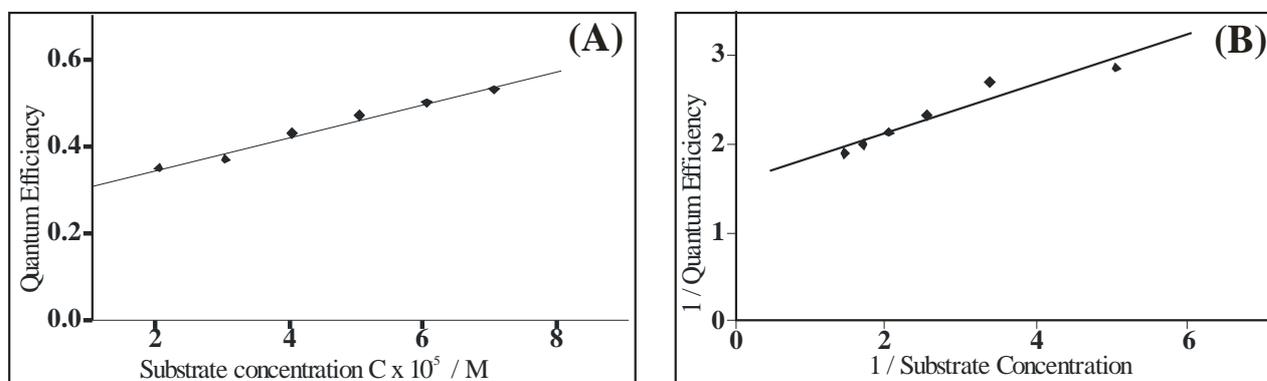
The quantum efficiency of the photoreaction of 2MT and MB has been determined using potassium ferrioxalate actinometer under various initial concentrations of 2MT. The plot of the  $\phi$  value and the initial concentration of the 2MT (**Figure 6(A)**) shows a straight line with positive slope suggesting the dependence of the quantum efficiency on the initial concentration of 2MT.

$$\Phi_{Prod} = \frac{k_2FG[2-MT]}{k_d+k_2[2-MT]} \quad \text{----- (1)}$$

$$\frac{1}{\Phi_{Prod}} = \frac{1}{FG} + \frac{k_d}{k_2FG[2-MT]} \quad \text{----- (2)}$$

$$\text{Where } F = \frac{k_p}{k_p+k_e} \text{ and } G = \frac{k_2}{k_{isc}+k_{sd}}$$

Equation 2 represents the dependence of the inverse of the quantum efficiency upon the inverse of the concentration of the substrate. As the concentration of 2MT increases, the plot of the inverse of the quantum efficiency Vs inverse of the concentration of the substrate (**Figure 6(B)**) shows the linearity with positive slope indicating that the electron transfer from the anion "S" of 2MT to the excited state cationic dye MB in the triplet excited state and no exciplex formation takes place during the photosensitized reaction [21]. Aromatic thiones were reported to populate efficiently their triplet excited states [22, 23]. The photo reaction product formation is monophotonic process as the quantum efficiency does not change with increase in light intensity.



**Figure 6** Plot of (A) quantum efficiency Vs substrate concentration (B) inverse of the quantum efficiency Vs inverse of the substrate concentration at 235 nm, 2MT:  $2 \times 10^{-5}$  mol L<sup>-1</sup> to  $8 \times 10^{-5}$  mol L<sup>-1</sup>, MB:  $1 \times 10^{-5}$  mol L<sup>-1</sup>, time interval: 10 mins, 100 W tungsten lamp, pH 11.

#### 2.4 Identification of the Photo Product

The reaction mixture after exposure to the visible radiation for 90 mins was analyzed for the reaction product, showing the presence of organic compound. The photoproduct shows only one absorbance maxima in UV spectrum at 225 nm having the molar absorptivity of  $3,375 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The UV spectrum of the photoproduct compares very well with the UV spectrum of the thiazole solution of the same concentration in the reaction condition. (**Table 2**).

The reaction product was isolated by extracting the exposed solution 4 times with 5 ml  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  was collected and evaporated to dryness and the product was dissolved in 5ml methanol. The methanolic solution of the product was used for the GC-MS analysis. A single peak was observed in the gas chromatogram suggesting that there is only one photoproduct. The RT (retention time) of the reaction product matches with the RT of the standard solution of thiazole. Lang and Jacobsen [24] have reported the formation of free thiol groups during the thiazoline hydrolysis. The mass spectrum (Figure 7) of the isolated product shows three main peaks. The peak at:  $m/z = 85$  ( $M+1$ , 100 %) which is also the base peak corresponds to  $[m+1]$  protonated molecular ion. The second and third peaks are observed at  $m/z = 83$  and  $m/z = 60$ . The triplet excited state molecule of 2MT undergoes decomposition to give thiazole as photoproduct. Gabriel et al [25] have observed the formation of N-acetylaminoethylmercaptan on hydrolysis under suitable conditions and a liberation of a thiol group.

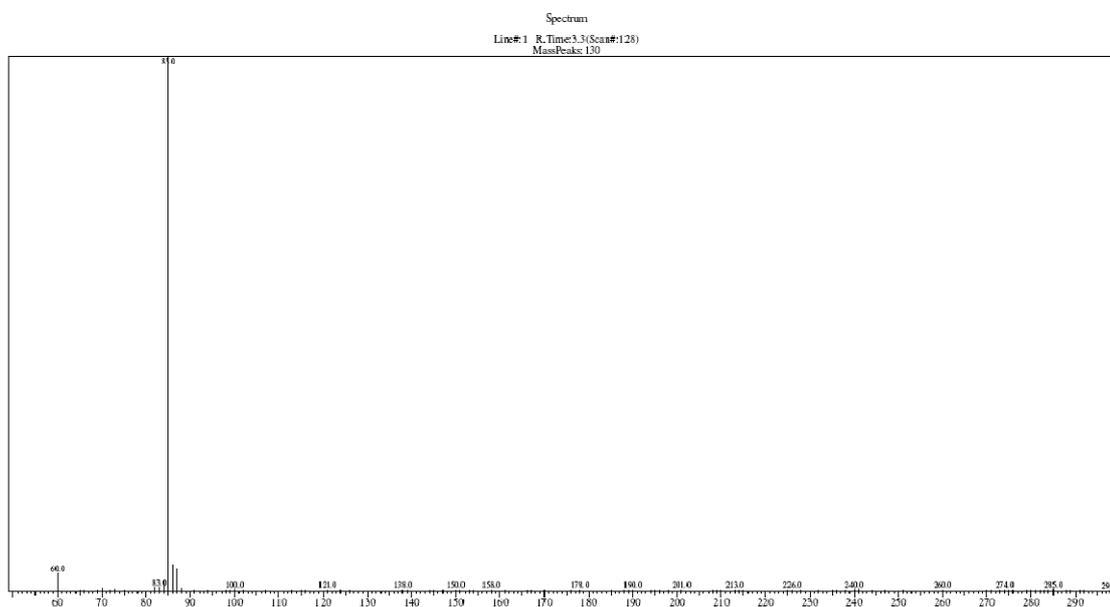


Figure 7 Mass spectra of the photoproduct of 2MT and MB on exposure

##### 2.4.1 Irradiation of Thiazole with Methylene Blue

The spectrum of a standard solution of thiazole and its mixture with methylene blue in aqueous alkaline medium were recorded in the range of 200 nm to 300 nm with time after exposure to the visible light. Thiazole shows  $\lambda_{\text{max}}$  at 235 nm and molar absorptivity  $3,715 \text{ L mol}^{-1} \text{ cm}^{-1}$  in the presence of MB before exposure but shows hypsochromic shift to 225 nm and decrease in the absorbance after exposure to the visible light. (**Fig 8**)

The thiazole free radical produces a thiazole molecule which interacts with the excited MB molecule on further exposure to the visible light and forms a DA complex which shows hypsochromic shift and absorbs at 225 nm as compared to the original thiazole  $\lambda_{\text{max}}$  at 235 nm and also shows lower molar absorptivity. The delocalization of the lone pair of the electron in the thiazole in the excited state is restricted due to the formation of 2MT – MB DA complex and the conjugation is less as compared to the original thiazole moiety. The excited DA complex is more stable in non polar solvent like ethanol and propanol, shows less hypsochromic shift as compared to the polar water solvent.

Uber et al. [26] have reported the photochemistry of the thiazole component of the vitamin B<sub>1</sub> and have shown that the decrease in the absorbance for the thiazole in the vitamin B<sub>1</sub> on photolysis by UV radiation is due to the change in the hydrogen of the 2 position of the thiazole ring rather than the breakdown of the thiazole ring.

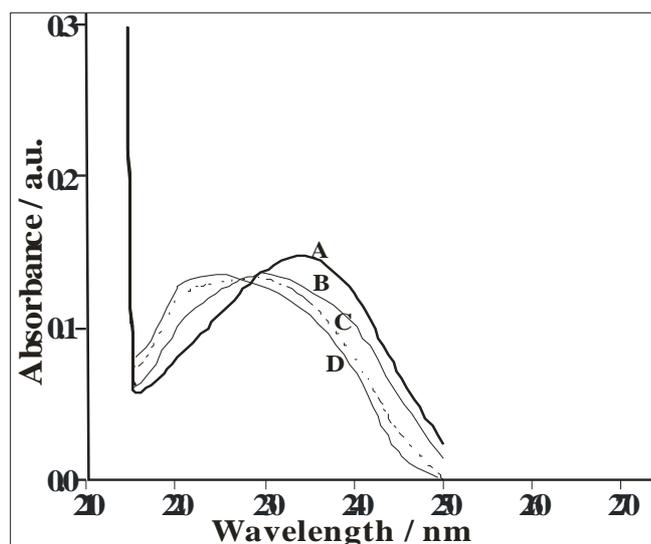


Figure 8 The absorbance spectra of thiazole with MB before and after exposure ((A) at  $T_0$ , (B) at  $T_{30}$ , (C) at  $T_{60}$ , (D) at  $T_{90}$ ), Thiazole:  $4 \times 10^{-5}$  M, MB:  $1 \times 10^{-5}$  M, 100 W tungsten lamp, pH 11

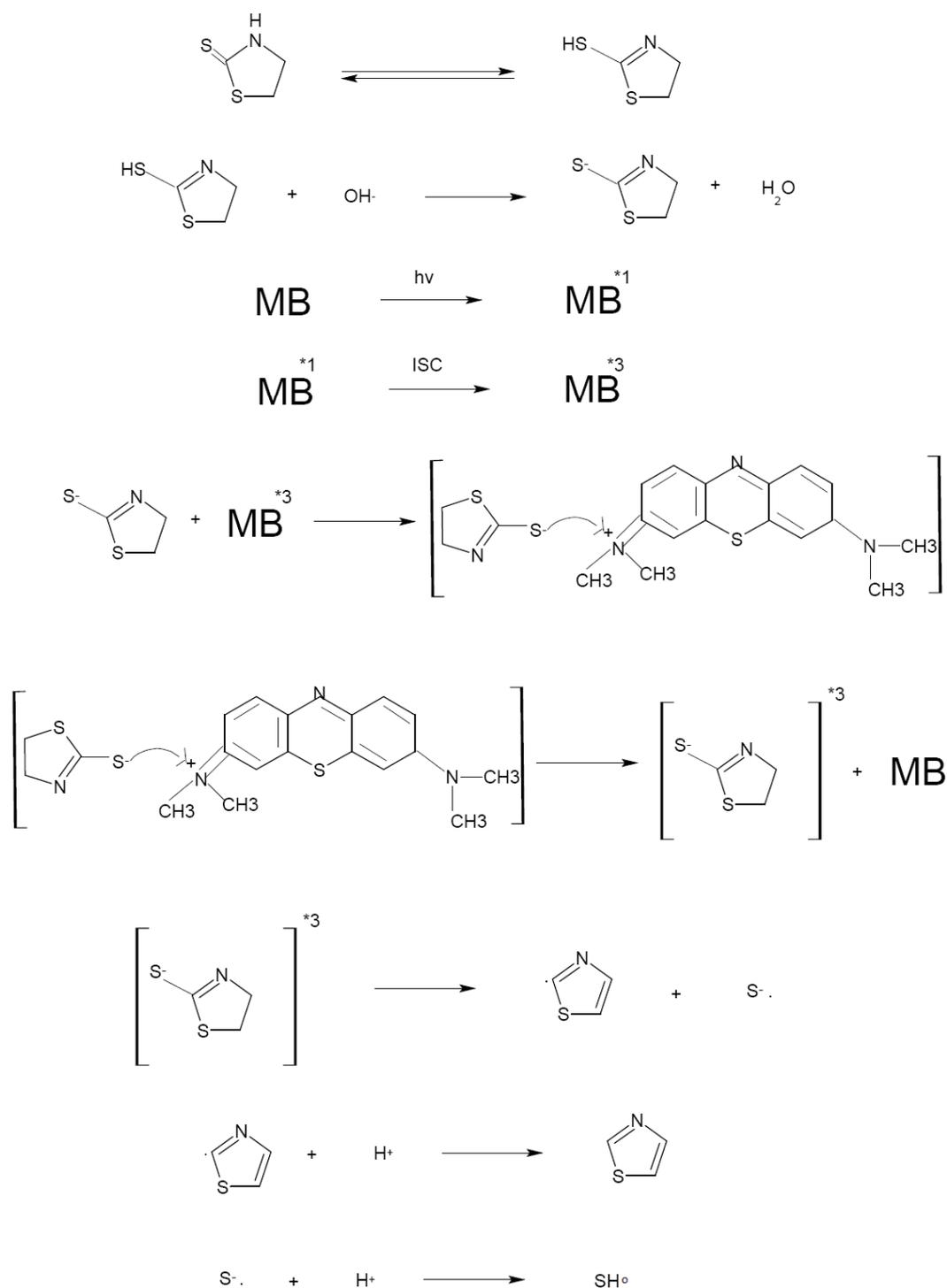
Table 2  $\lambda_{max}$  and molar absorptivity of 2MT, photoproduct and thiazole at 11 Ph

Species Present	$\lambda_{max}$	Molar absorptivity ( $L \text{ mol}^{-1} \text{ cm}^{-1}$ )
2-Mercaptothiazoline	235 nm	17,080
Photo Product	225nm	3,375
Thiazole	235 nm	3,715
Thiazole + MB before exposure	235 nm	3,662.5
Thiazole + MB after exposure ( For 90 min)	225 nm	3,375

### 2.5 Mechanism

The 2MT exists as protonated and deprotonated form at different pH and have  $\lambda_{max}$  below 400 nm which do not absorb visible light and are photo stable. The protonated form of 2MT undergoes deprotonation in the alkaline medium and the anion of the protonated form undergoes photoreaction with cationic dye MB. Methylene blue (MB) has  $\lambda_{max}$  at 665 nm which absorbs visible radiation and forms singlet excited molecule. The singlet excited state MB gives triplet excited state of the MB on ISC. The mercapto substituent of 2MT has high reactivity toward the electrophilic reaction [27]. The cationic dye methylene blue accepts electron from anion of the protonated form and transfers energy to 2MT anion (dipole-dipole energy transfer mechanism). The 2MT anion goes to triplet excited state and MB comes back to the ground state (Scheme 1).

Freeman *et. al.* [28] have reported that if the bond fission energy is lower than the triplet excited state then the product formation can occur directly from the triplet excited state of 2MT and the process should be homolytic bond fission. The C-S bond is of weak energy rendering bond which shows the homolytic bond cleavage on photolysis [29]. The formation of the thiazole radical and sulphur radical anion is due to homolytic fission of C-S bond. Malouki *et.al.* [30] have reported the direct photolysis of 2-Mercaptobenzothiazole in water involves the triplet excited state and benzothiazolyl radical as primary intermediates. The thiazole radical will abstract hydrogen from a hydrogen donor to form thiazole. The sulphur radical anion will react with a proton to form a  $\text{SH}^\circ$  radical. The higher value of the quantum efficiency for the reaction suggest that excited species undergoes decomposition more efficiently than deactivation. The concentration of 2MT anion decreases as the reaction proceeds.



Scheme 1. Mechanism of 2MT degradation

**CONCLUSION**

2MT is more toxic compare to the thiazole and the photosensitized reaction of 2MT with MB use to convert 2MT to less toxic thiazole by dipole-dipole energy transfer mechanism. The irradiation of MB with visible light excites it to singlet excited state which gives triplet excited state on ISC which interacts with 2MT anion and transfers its energy to 2MT anion and comes back to ground state. The triplet excited state of 2MT anion gives thiazole radical and sulphur radical which gives thiazole and SH° radical as a photoproducts. The first-order kinetic constant

(apparent k) of the photodecomposition reaction of 2MT is independent of the concentration of 2MT and MB but dependent on the pH of the solution and light intensity. The plot of  $1/\phi$  Vs  $1/C$  suggests triplet – triplet energy transfer from the sensitizer to substrate without exciplex formation.

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