Chapter 3

Photosensitized Electron Transfer Reaction of 2-Thiobarbituric Acid and Methylene Blue

Abstract

The photosensitized reaction of 2-Thiobarbituric acid (2-TBA) with methylene blue (MB) in alkaline medium using visible light has been studied. 2-TBA exists in protonated and deprotonated form in equilibrium in alkaline medium. Photosensitized electron transfer from the deprotonated 2-TBA to excited state MB takes place and the energy is transferred to 2-TBA molecule which undergoes chemical reaction. The interconversion of protonated form to deprotonated form during the reaction is observed. The rate of the reaction has been calculated and the effect of pH, concentration of the sensitizer, the light intensity on the rate of the reaction has been studied. The quantum efficiency of the photo chemical 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.

3.1 Introduction

Thiobarbituric acid is a condensation product of malonic acid and thiourea which is closely related to barbituric acid. Barbiturates are known to have hypnotic properties and are used as active moiety on central nervous system. Thiobarbituric acid differs from barbituric acid only by the presence of a sulfur atom instead of an oxygen atom at the number 2 carbon. It is the parent compound of a class of drugs, the thiobarbiturates, which are analogous in their effects to barbiturates.

Biological activity of the 2-TBA molecule is mainly related to the tautomerism and the nature of the substituent. 2-TBA shows two pKa values one in the range 2.10 – 2.25 and a second in the range 10.55 – 10.72. The lower value corresponds to the molecular equilibrium between the N – protonated enol form and the neutral form, while the higher pKa is attributed to the equilibrium between neutral and anionic forms [9].

Thialbarbital (Intranarcon) is a barbiturate derivative synthesized in the 1960s. It has sedative effects, and was used primarily as the surgical anaesthesia. Thialbarbital is short acting and has less of a tendency to induce respiratory depression than other barbiturate derivatives such as pentobarbital. Thiobarbital is a drug which is a barbiturate derivative. It is the thiobarbiturate
analogue of barbital. Thiobutabarbital (Inactin, Brevinarcon) is a short-acting barbiturate derivative synthesized in the 1950s. It has sedative, anticonvulsant and hypnotic effects, and is still used as veterinary medicine for induction as surgical anaesthesia. Thiamylal (Surital) is a barbiturate derivative synthesized in the 1950s. It has sedative, anticonvulsant and hypnotic effects, and is used as a strong but short acting sedative. Thiamylal is still in current use, primarily for induction in surgical anaesthesia or as an anticonvulsant to counteract side effects from other anaesthetics. It is the Thiobarbiturate analogue of secobarbital.

2-TBA is a substituted mercaptopyrimidine with three mobile H atoms and 10 possible tautomeric forms. (Fig 1.1) 2-TBA is a heterocyclic organic compound and is used as a reagent in assaying malondialdehyde [1]. It is used in a neuraminidase activity and inhibition assay. It shows high reactivity, especially with unsaturated aldehydes [2-4]. Thiobarbituric acid has been used as a radical probe and in the dimerization of cysteine in vitro and phototoxicity of pyrazinamide reaction [5].

**Isomers of 2-TBA (X = S)**

A number of procedures have been reported for the measurement of fat oxidation for animal and vegetable fat using thiobarbituric acid [6]. 2-TBA - malonaldehyde reaction has been used as a measure of antioxidant effectiveness in pharmaceutical oils [7]. 2-TBA assay has been widely applied for the measurement of lipid oxidation in food and also in biological tissues (Esterbauer and Cheeseman, 1990).
2-TBA reactions are quantified by colorimetry or fluorimetry. 2-TBA reacts with a wide variety of chemical species to produce a pink to red colour [8] and this reaction has been used to develop colorimetric and fluorometric methods for determination. Domagalska et. al. [10] have reported the electronic and spectral properties of the conjugated polyenes with electron-accepting 1, 3-dialkyl-2-thiobarbituric acid.

Due to its multipurpose use, thiobarbiturate derivatives are frequently detected in both waste water treatment plant and surface water. In the last decade photochemical study of such compounds has been a topic of keen interest and an extensive work has been reported on the photochemical study of substituted thiobarbiturates.

5-Ethyl- and 5-allyl-5-(1-methyl-3-oxobutyl) barbituric acids and ethyl- and 5-allyl-(1-methyl-3-oxobutyl)-2-thiobarbituric acids have been shown to decompose via a reverse Michael type reaction in alkaline conditions. 2- Thiobarbituric acid derivatives decomposed more rapidly than their corresponding barbituric acid analogs, and the 5-allyl derivative decomposed faster than the 5-ethyl compound in each case [11].

Hunkset et. al. [12] have reported that the double deprotonation of the thiobarbituric acid leads to the formation of a macrocyclic complex and it undergoes intermolecular hydrogen bonding to give a different type of polymeric tape structure.

Aoyama et. al. [13] have reported that the photochemical reaction of the barbital and its derivatives gave Norrish type II reaction products and have also compared the photochemical reactivities of barbital with other nitrogen containing carbonyl compound. The photolysis of the aqueous solution of pyrimidines produces radicals by one electron reduction involving hydrated electrons. The structures of the radicals were assigned on the basis of their EPR spectrum.

Owing to the interest in the environment protection, the photo-degradation may play an important role in their elimination from aquatic environment. The photodegradation study of 2-TBA using cationic dye methylene blue as a sensitizer in the presence of the visible light is not reported elsewhere.

The present study reports the photochemical reaction of 2-TBA in the aqueous alkaline medium on irradiation with visible light. The cationic dye, methylene blue has been used as photo sensitizer. There are very few reports in the literature for the sensitized study of 2-TBA. The reaction is monitored by measuring the spectrum change of 2-TBA. The kinetics of the photo degradation 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 calculate the quantum efficiency and to know whether the reaction is monophotonic or biphotonic. The effect of the oxygen and free radical scavenger has been studied on the reaction. The mechanism of the photosensitized reaction has been suggested. Methylene blue has been used as a photosensitizer in the present study which has also been used as sensitizer in a number of photochemical reactions [14-17]. It shows two different type of energy transfer process e.g. electron transfer reactions, exciplex formations and energy transfer to triplet O\(_2\) to convert it to singlet oxygen for photo-oxygenation.

### 3.2 Results

#### 3.2.1. Spectral characteristics:

The UV spectrum of the pure 2-TBA (5 X 10\(^{-5}\) M) was recorded at different pH, to determine the different species present at the different pH of the aqueous solution. The pH of the solution was maintained using suitable concentration of HCl or NaOH in the solution.

The initial spectrum of 2-TBA (5 X 10\(^{-5}\) M) in the aqueous acidic solution is represented by the dash line in Fig 3.2 which exhibits two well-defined maxima one at 285 nm (\(\varepsilon = 24,000\) L mol\(^{-1}\) cm\(^{-1}\)) and a second at 235 nm (\(\varepsilon = 9,000\) L mol\(^{-1}\) cm\(^{-1}\)) at pH 2. The cationic and neutral species of 2-TBA are in equilibrium between the pH value 2 to 6.

2-TBA shows two maxima (Fig 3.2) one at 235 nm [N4 or N5 or N10] (\(\varepsilon = 13,000\) L mol\(^{-1}\) cm\(^{-1}\)) and a second at 285 nm [N1] (\(\varepsilon = 8,500\) L mol\(^{-1}\) cm\(^{-1}\)) at pH 12 (continuous line).

2-TBA in alkaline solution shows higher absorbance at 235 nm and lower absorbance at 285nm, while the protonation in the acidic solution shows higher molar absorptivity value at 285 nm and lower molar absorptivity value at 235 nm. The dominant peak in the acidic medium is at 285 nm which shifts to the shorter wave length at 235 nm and becomes the dominant peak in alkaline medium at pH 12. (Fig 3.2)

The \(\lambda_{\text{max}}\) and molar absorptivities of the different species of 2-TBA are quoted in Table 3.1. The spectral changes are reversible by changing the pH of the solution.

The exposure of the solution containing only 2-TBA (5 x 10\(^{-5}\) M) in the pH range 2 – 12 to visible radiation does not result in the change of the original spectrum of the solution. The direct photolysis of 2-TBA on irradiation by the visible light does not occur in the acidic or in the alkaline medium and 2-TBA is photo stable.
Fig 3.2 Spectrum of the 2-TBA (5 x 10^{-5} M) in the acidic and in the alkaline medium

(a) In acidic medium at pH 2 (----)

(b) In alkaline medium at pH 11.5 (—)
Table 3.1 \( \lambda_{\text{max}} \) and molar absorptivity of the 2-TBA species in the acidic and alkaline medium

<table>
<thead>
<tr>
<th>2-TBA Species Present</th>
<th>pH of the solution</th>
<th>( \lambda_{\text{max}} )</th>
<th>Molar absorptivity (L mol(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTBA [N4 or N5 or N10]</td>
<td>2 to 6</td>
<td>285 nm</td>
<td>24000</td>
</tr>
<tr>
<td>H2TBA+</td>
<td></td>
<td>235 nm</td>
<td>9000</td>
</tr>
<tr>
<td>HTBA [N4 or N5 or N10]</td>
<td>8 to 12</td>
<td>235nm</td>
<td>13000</td>
</tr>
<tr>
<td>TBA- [N1]</td>
<td></td>
<td>285nm</td>
<td>8500</td>
</tr>
</tbody>
</table>

Table 3.1 \( \lambda_{\text{max}} \) and molar absorptivity of the 2-TBA species in the acidic and alkaline medium, Substrate: 2-TBA \((5 \times 10^{-5} \text{ M})\), In Acid Medium: pH 2, In Alkaline Medium: pH 11.

The reaction mixture containing 2-TBA \((5 \times 10^{-5} \text{ M})\) and MB \((1.5 \times 10^{-5} \text{ M})\) was prepared and the pH of the solution was maintained between 2 to 12. The solutions were kept in the dark and their spectrum were recorded which matched with the original spectrum of the 2-TBA. 2-TBA and MB do not interact in the ground state.

The reaction mixture containing 2-TBA \((5 \times 10^{-5} \text{ M})\) and MB \((1.5 \times 10^{-5} \text{ M})\) maintained at different pH between 2 to 12 were exposed to the visible radiation and the spectrum of the solutions were recorded against the reagent blank. The reaction mixture does not undergo photo reaction in the pH range 2 – 6 but it undergoes photo reaction in the presence of MB in the pH range of 8 – 12. 2-TBA is photo stable in the acidic medium and does not undergo photoreaction with MB when exposed to the visible radiation but it shows photoreaction in the presence of MB used as a sensitizer in the alkaline medium.
The absorption spectra of the photosensitized reaction of 2-TBA with MB

Fig 3.3 Absorption spectra of the photosensitized reaction of 2-TBA with MB on exposure

Substrate: 2-TBA (5 x 10^{-5} M),

Sensitizer: MB (1.5 x 10^{-5} M),

Time interval: 10 mins,

Source: 100 W tungsten lamp, pH 11
The absorption band at 235 nm and at 285 nm shows decrease in the absorption with time when the reaction mixture is exposed to the visible radiation and the absorbance were recorded with time. The changes of the absorption spectrum were plotted against time which show decrease at the $\lambda_{\text{max}}$ 235 nm and 285 nm. (Fig 3.3) The spectrum shows increase in the absorbance at 220 nm with time and an isobestic point was not observed. The product of photo-reaction absorbs at a shorter wavelength in comparison to the starting material.

3.2.2. Determination of the rate constant

The progress of the photosensitized reaction was monitored by recording UV spectra of the 2-TBA (5 x $10^{-5}$ M) with MB (1.5 x $10^{-5}$ M) in the range 200 - 400 nm. The spectrum of 5 ml aliquot of the exposed solution, withdrawn after 10 min time intervals has been recorded in the range of 200 nm – 400 nm against a reagent blank. The absorbance of the solution was also measured at 235 nm and 285 nm.

The absorbance decreases at both the $\lambda_{\text{max}}$ of 2-TBA and becomes constant after 90 min exposure to the visible light indicating the completion of the reaction. The absorbance shows different rate of decrease of 2-TBA species having $\lambda_{\text{max}}$ at 235 nm and 285 nm respectively. It is observed that the absorbance at 285 nm decreases at a faster rate than at 235 nm. The decrease of the absorbance with time for 2-TBA at the $\lambda_{\text{max}}$ 235 nm and 285 nm has been used to calculate the rate of the reaction. The results of a typical run for the change in the absorbance of 2-TBA with time have been presented in Fig 3.4.

The change in the absorbance with time has been used for the calculation of the rate of the reaction. The reaction follows the first order reaction kinetics as the plot of $2 + \log \text{OD}$ (optical density) vs. time (Fig 3.5) was found to be a straight line with a positive slope. The rate constant of the reaction has been determined by the expression:

$$\text{Rate constant} = 2.303 \times \text{slope}$$
Absorption Vs time plot of the photosensitized reaction of 2-TBA with MB

![Absorption Vs time plot of the photosensitized reaction of 2-TBA with MB](image)

**Fig 3.4 Absorption Vs time plot of the photosensitized reaction of 2-TBA with MB on exposure.**

- **Substrate:** 2-TBA ($5 \times 10^{-5}$ M),
- **Sensitizer:** MB ($1.5 \times 10^{-6}$ M),
- **Time interval:** 10 mins,
- **Source:** 100 W tungsten lamp
Fig 3.5 $2 + \log OD$ vs Time plot of the photosensitized reaction of 2-TBA with MB on exposure.

2-TBA ($5 \times 10^{-5}$M)

MB ($1.5 \times 10^{-5}$M)

Time interval: 10 mins

Source: 100 W tungsten lamp
3.2.2.1 Effect of the pH on the rate of the reaction:

The spectrum of the pure 2-TBA solution ($5 \times 10^{-5}$ M) was recorded at different pH in the range of 200 nm – 400 nm and the effect of the pH on the rate of the photosensitized reaction was carried out by changing the pH of the reaction mixture between 2 – 12 and the calculations for the rate of the reaction were carried out by measuring the absorbance at $\lambda_{\text{max}}$ 235 nm and 285 nm at different time intervals. (Table 3.2)

The photosensitized reaction does not take place between the pH value 2 – 6 and increases up to the pH of the solution is 10 and then becomes constant (Fig 3.6). The subsequent studies were carried out at pH 11.

The spectrum of the exposed reaction mixture between the pH value 2 to 6 remains the same as the control solution. The species of 2-TBA present in the acidic medium do not undergo the photosensitized reaction. The species present in the alkaline medium undergo photochemical reaction. The change in the spectrum in the alkaline medium shows decrease in the absorbance at the $\lambda_{\text{max}}$ 235 and 285 nm.

The pH of the reaction mixture influences both methylene blue and 2-TBA. Watts et al [18] has reported that the methylene blue sensitized reactions are more efficient at pH greater than 8.

The neutral species of HTBA can be protonated or de-protonated depending on the pH value of the solution [19].

\[
\text{HTBA} + \text{H}^+ \leftrightarrow \text{H}_2\text{TBA}^+ \quad (\text{pH} \ 2 - 6)
\]

\[
\text{HTBA} \leftrightarrow \text{H}^+ + \text{TBA}^- \quad (\text{pH} \ 8 - 10)
\]

2-TBA exists as $\text{H}_2\text{TBA}^+$ and HTBA forms between pH value 2 – 6 which show $\lambda_{\text{max}}$ at 235 nm ($\varepsilon = 9,000$ L mol$^{-1}$ cm$^{-1}$) and at 285 nm ($\varepsilon = 24,000$ L mol$^{-1}$ cm$^{-1}$) respectively. 2-TBA exists as HTBA and TBA$^-$ forms between pH 8 – 12 which show $\lambda_{\text{max}}$ at 235 nm ($\varepsilon = 13,000$ L mol$^{-1}$ cm$^{-1}$) and at 285 nm ($\varepsilon = 8,500$ L mol$^{-1}$ cm$^{-1}$) respectively. The rate of the photosensitized reaction increases with increase in pH and becomes constant at pH 10 suggests that only anionic species of 2-TBA undergo photo reaction.

It is observed that the absorbance at the $\lambda_{\text{max}}$ 285 nm decreases faster than absorbance at the $\lambda_{\text{max}}$ 235 nm. It appears TBA$^-$ undergoes degradation and HTBA in equilibrium with TBA$^-$ is converted...
to TBA$^-$ as its concentration decreases. The rate of the degradation of TBA$^-$ is faster than the rate of the conversion of HTBA to TBA$^-$.

**Table 3.2** Effect of pH on the rate of the reaction at 285 nm

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>Rate of the Reaction (K x $10^{-2}$ mole / L min [Avg K ± 0.4])</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.11</td>
</tr>
<tr>
<td>4</td>
<td>0.11</td>
</tr>
<tr>
<td>7.8</td>
<td>0.20</td>
</tr>
<tr>
<td>10.53</td>
<td>2.59</td>
</tr>
<tr>
<td>11</td>
<td>2.59</td>
</tr>
<tr>
<td>11.52</td>
<td>2.59</td>
</tr>
</tbody>
</table>

**Table 3.2** Effect of the pH on the rate of the reaction measured at 285 nm. Substrate: 2-TBA ($5 \times 10^{-5}$ M), Sensitizer: MB ($1.5 \times 10^{-5}$ M), Source: 100 W tungsten lamp
Effect of the pH on the rate of the reaction

![Graph showing the effect of pH on the rate of reaction.]

Fig 3.6 Effect of the pH on the rate of the reaction measured at 285 nm.

2-TBA ($5 \times 10^{-5}$ M)

MB ($1.5 \times 10^{-5}$ M)

Time interval: 10 mins

Source: 100 W tungsten lamp
Effect of the concentration of the sensitizer on the rate of the reaction:

The effect of the concentration of MB on the rate of the photosensitized reaction has been studied. The study was carried out by varying the concentration of MB in the range of $4 \times 10^{-6}$ M to $3 \times 10^{-5}$ M.

The 2-TBA degradation increased initially with the increase of MB concentration in the reaction mixture, but decreased as the MB concentration reached above a threshold level. The results indicate that $1.5 \times 10^{-5}$ M MB had an optimal content to achieve the best performance under the experimental condition. *(Fig 3.7)*

2-TBA has its $\lambda_{max}$ below 400 nm and is not photo degraded directly by the visible light. Methylene blue absorbs visible radiation at 665 nm and gets excited, which on collision with the 2-TBA, transfers energy to it. The number of the excited sensitizer molecules increases up to a limiting value of the concentration of the sensitizer, the rate increases initially and then becomes constant but at the higher concentration of the sensitizer the rate of the reaction slightly decreases due to the self deactivation of the sensitizer molecule by intermolecular collision.
Effect of the sensitizer concentration on the rate of the reaction

Fig 3.7 Effect of the sensitizer concentration on the rate of the reaction at 11 pH.

- 2-TBA (5 x 10^{-5} M)
- MB (4 x 10^{-6} M to 3 x 10^{-5} M)

Time interval: 10 mins

Source: 100 W tungsten lamp
3.2.2.3 Effect of the concentration of the substrate on the rate of the reaction

The effect of the initial concentration of 2-TBA on the rate of the reaction was studied. The rate of the reaction has been calculated with the different initial concentration of the substrate in the range of \((4.0 - 8.0) \times 10^{-5}\) M (Table 3.3) which remains constant in the concentration range shows that the reaction is independent of the initial concentration of the substrate. (Fig 3.8)

The half life time of the reaction is also calculated at different concentration of the substrate and \(t_{1/2}\) value is constant over the above range of the substrate concentration. This suggests that the photochemical reaction is of the first order.

### Table 3.3 Effect of the concentration of substrate on the rate of the reaction at 285 nm

<table>
<thead>
<tr>
<th>Concentration of Substrate (C \times 10^{-5})</th>
<th>Rate of the Reaction ((K \times 10^{-2})) mole / L min [Avg K ± 0.4]</th>
<th>(t_{1/2}) L min / mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>5.76</td>
<td>12.03</td>
</tr>
<tr>
<td>3.4</td>
<td>5.76</td>
<td>12.03</td>
</tr>
<tr>
<td>3.5</td>
<td>5.76</td>
<td>12.03</td>
</tr>
<tr>
<td>3.7</td>
<td>5.76</td>
<td>12.03</td>
</tr>
<tr>
<td>3.9</td>
<td>5.76</td>
<td>12.03</td>
</tr>
</tbody>
</table>

Table 3.3 Effect of the substrate concentration on the rate of the reaction at 11 pH, Substrate: 2-TBA \((3 \times 10^{-5}\) M to \(4 \times 10^{-5}\) M), Sensitizer: MB \((1.5 \times 10^{-5}\) M), Time interval: 10 mins, Source: 100 W tungsten lamp
Effect of the substrate concentration on the rate of the reaction

![Graph showing the effect of substrate concentration on the rate of reaction.](image)

**Fig 3.8** Effect of the substrate concentration on the rate of the reaction at 11 pH.

2-TBA ($3.3 \times 10^{-5}$ M to $3.9 \times 10^{-5}$ M)

**MB** ($1.5 \times 10^{-5}$ M)

Time interval: 10 mins

Source: 100 W tungsten lamp
3.2.2.4 **Effect of the light intensity on the rate of the reaction**

The solutions of the different concentration of the substrate [2-TBA] and the sensitizer MB were prepared in the aqueous alkaline solution and irradiated with the visible light. The rate of the reaction was calculated. *(Table 3.4)*

The increase of the light intensity [Einstein / second (E/s)] shows positive effect and the rate 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 rate of the reaction also increases. A linear relationship has been observed between the light intensity and the rate of the reaction. *(Table 3.4)*

**Table 3.4** **Effect of the Light Intensity on the rate of the reaction and on the quantum efficiency**

<table>
<thead>
<tr>
<th>Light Intensity $(1 \times 10^{8})$ E/s</th>
<th>Rate of the Reaction at 310 nm $(K \times 10^{-2})$ mole / L min [Ave $K \pm 0.5$]</th>
<th>Quantum efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.94</td>
<td>0.3236</td>
</tr>
<tr>
<td>10</td>
<td>1.84</td>
<td>0.3223</td>
</tr>
<tr>
<td>15</td>
<td>2.62</td>
<td>0.3216</td>
</tr>
<tr>
<td>20</td>
<td>3.46</td>
<td>0.3253</td>
</tr>
<tr>
<td>25</td>
<td>4.55</td>
<td>0.3263</td>
</tr>
</tbody>
</table>

**Table 3.4** **Effect of light intensity on quantum efficiency and on the rate of the reaction at 11 pH, Substrate: 2-TBA $(5 \times 10^{-5})$, Sensitizer: MB $(1.5 \times 10^{-5} \text{ M})$, Time interval: 10 mins, Source: 100 W tungsten lamp
3.2.2.5 Effect of the anaerobic condition on the rate of the reaction & the quantum efficiency

The reaction was studied in the anaerobic condition to observe the effect of the oxygen on the rate of the reaction.

The solutions of the different concentration of the substrate [2-TBA] and the sensitizer MB were prepared in the aqueous alkaline medium. The reaction mixtures were de-aerated by purging with purified nitrogen for 30 min via a needle through the cap. The maximum deoxygenated reaction mixtures of the 2-TBA and the MB were exposed to the visible light.

The rate of the reaction was calculated. The rate of the reaction does not show change and remains the same 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. This suggests that the singlet oxygen does not participate in the photosensitized reaction. (Table 3.5)

**Table 3.5** Effect of the anaerobic condition on the rate of the reaction and on the quantum efficiency at 285 nm

<table>
<thead>
<tr>
<th>2-TBA</th>
<th>Rate of the reaction in aerobic aqueous alkaline medium</th>
<th>Rate of the reaction in anaerobic aqueous alkaline medium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K \times 10^{-2}$ mole / L min</td>
<td>$K \times 10^{-2}$ mole / L min</td>
</tr>
<tr>
<td>235 nm</td>
<td>2.59</td>
<td>0.83</td>
</tr>
<tr>
<td>285 nm</td>
<td>1.23</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 3.5 Effect of the anaerobic condition on the rate of the reaction and on the quantum efficiency at 11 pH, Substrate: 2-TBA ($5 \times 10^{-5}$ M), Sensitizer: MB ($1.5 \times 10^{-5}$ M), Time interval: 10 mins, Source: 100 W tungsten lamp
3.2.2.6 Effect of the free radical scavenger

The effect of the solvent used as free radical scavenger on the photo sensitized reaction of 2-TBA was studied by changing the medium from aqueous alkaline to methanolic alkaline.

The solutions of the the different concentration of substrate [2-TBA] and the sensitizer MB were prepared in the alkaline methanolic solution and irradiated with the visible light. The two isomers of 2-TBA N1 and N10 show \( \lambda_{\text{max}} \) at 235 nm and at 285 nm are present approximately in the same concentration in the alkaline methanolic solution. The rate of the reaction was calculated.

The photochemical reaction doesn’t show change in the alkaline methanolic solvent except the rate of the reaction slightly decreases suggests that methanol does not have free radical scavenger effect and there is no free radical formation during the reaction. Similar results were obtained using NaN\(_3\) as a free radical scavenger. (Table 3.6)

The change of medium from water to methanol, ethanol and propanol shows that the rate of the reaction decreases, it appears that the rate of the reaction depends upon the polarity of the medium. The electron transfer reaction between 2-TBA anion and excited state molecule of MB is more efficient in higher polar solvent while deactivation of excited 2-TBA\(^-\) is more efficient in non polar solvent.

Table 3.6 Effect of the free radical scavenger on the rate of the reaction and on the quantum efficiency at 285 nm

<table>
<thead>
<tr>
<th>Rate of the reaction in aqueous alkaline medium K ( \times 10^{-2} ) mole / L min</th>
<th>Rate of the reaction in alkaline methanolic medium K ( \times 10^{-2} ) mole / L min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.68 ( at 235 nm )</td>
<td>2.54 ( at 235 nm )</td>
</tr>
<tr>
<td>1.42 ( at 285 nm )</td>
<td>1.36 ( at 285 nm )</td>
</tr>
</tbody>
</table>

Table 3.6 Effect of the free radical scavenger on the rate of the reaction and on the quantum efficiency at 11 pH, Substrate: 2-TBA \( (5 \times 10^{-5} \) M), Sensitizer: MB \( (1.5 \times 10^{-5} \) M), Time interval: 10 mins, Source: 100 W tungsten lamp
3.3 The quantum efficiency

The quantum efficiency of the photo reaction of 2-TBA and MB has been calculated using Potassium ferrioxalate actinometer and was determined with a number of initial concentration of 2-TBA.

The graph of quantum efficiency and different initial concentration of 2-TBA shows a horizontal relationship. The quantum yield of the reaction is independent of the substrate concentration. (Fig 3.9)

The plot of the inverse of the quantum yield versus the inverse of the substrate concentration is horizontal with zero slope suggests that the singlet – singlet energy transfer takes place. The singlet excited state of the cationic dye methylene blue transfers energy to the substrate molecule and a singlet excited state of the 2-TBA is formed. The graph also indicates that the exciplex formation does not take place and the decomposition of the singlet excited state of the substrate molecule takes place [20]. (Fig 3.10)

<table>
<thead>
<tr>
<th>Substrate Concentration (C × 10⁻⁴ M)</th>
<th>Quantum Efficiency (Φ)</th>
<th>Inverse of substrate concentration (C × 10⁴)</th>
<th>Inverse of quantum efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>0.3216</td>
<td>3.125</td>
<td>3.109</td>
</tr>
<tr>
<td>0.33</td>
<td>0.3219</td>
<td>3.03</td>
<td>3.107</td>
</tr>
<tr>
<td>0.34</td>
<td>0.3217</td>
<td>2.94</td>
<td>3.108</td>
</tr>
<tr>
<td>0.37</td>
<td>0.3223</td>
<td>2.70</td>
<td>3.103</td>
</tr>
<tr>
<td>4.00</td>
<td>0.3221</td>
<td>2.50</td>
<td>3.105</td>
</tr>
</tbody>
</table>

Table 3.7 Different initial substrate concentration and quantum efficiency at 11 pH, Substrate: 2-TBA (5 x 10⁻⁵ M), Sensitizer: MB (1.5 x 10⁻⁵ M), Time interval: 10 mins, Source: 100 W tungsten lamp
Fig 3.9 Plot of quantum efficiency Vs substrate concentration at 11 pH.

- 2-TBA ($3.3 \times 10^{-5}$ M to $3.9 \times 10^{-5}$ M)
- MB ($1.5 \times 10^{-5}$ M)

Time interval: 10 mins

Source: 100 W tungsten lamp
Fig 3.10 Plot of inverse of the quantum efficiency Vs inverse of the substrate concentration

- TBA (3.3 x 10^{-5} M to 3.9 x 10^{-5} M)
- MB (1.5 x 10^{-5} M)

Time interval: 10 mins

Source: 100 W tungsten lamp
3.3.1 Effect of the light intensity on the quantum efficiency

The quantum efficiency of the reaction of 2-TBA with MB as a sensitizer was determined using light intensity in the range 5 – 25 E/s.

The solutions of the different concentration of the substrate [2-TBA] and the sensitizer MB were prepared in the aqueous alkaline solution and irradiated with the visible light of different intensity for the fixed time intervals. The quantum efficiency of the photoreaction has been calculated.

The $\phi$ value remains constant in this range of the light intensity. The graph of $\phi$ value vs light intensity is horizontal line with zero slope suggesting a monophotonic reaction. (Fig 3.11)
Fig 3.11 Plot of light intensity Vs quantum efficiency at 11 pH.

2-TBA (5 x 10^{-5} M)

MB (1.5 x 10^{-5} M)

Time interval: 10 mins
3.4 Product study

The $\lambda_{\text{max}}$ and molar absorptivity of the photo product of the reaction of 2-TBA and MB in aqueous alkaline solution has been evaluated under experimental condition. The molar absorptivity of the substrate and product has been calculated by measuring the absorbance of a number of known concentration solutions.

The experimental study shows that photo reaction does not involve singlet oxygen. The substrate molecule does not undergo oxidation. The effect of the free radical scavenger shows that there is absence of the free radical formation in the reaction. The singlet excited state of the substrate molecule directly undergoes degradation forming the product.

The analysis of the reaction mixture for photo product does not show the presence of organic compound. The qualitative test for $\text{SO}_4^{2-}$ and $\text{S}^2$ was found negative with $\text{BaCl}_2$ solution and lead acetate respectively. The qualitative analysis, spectrophotometric analysis and IC analysis suggest the presence of SCN which appears to be the only photo product.

**Test for the SCN$^-$ ion:** The reaction mixture was further tested for SCN$^-$ ion with FeCl$_3$ solution which gave an orange colouration which absorbed at 440 ± 2 nm. This was further confirmed by preparing a standard solution of KCNS and MB of the same concentration as in the experiment with 2-TBA and MB at 11 pH. The spectrum of the solution of SCN with MB was measured before exposure and after the exposure to light. (Fig 3.12)

The absorbance spectra of KCNS with MB of the same concentration range as of 2-TBA before and after irradiation shows the absorbance maximum at 225 nm and 220 nm having the molar absorptivity of 2,472 L mol$^{-1}$ cm$^{-1}$ and 2,674 L mol$^{-1}$ cm$^{-1}$ respectively. (Table 3.8)

**IC analysis for Thiocyanate determination:** The sensitizer MB was extracted by charcoal and the remaining reaction mixture was collected and used for IC analysis (the parameter of IC analysis described in chapter 2). Fig 3.13 shows the IC analysis spectrum of std. SCN$^-$ (100 ppm) in water sample. Fig 3.14 shows the IC analysis spectrum of reaction photo product of 2-TBA. The RT of the reaction product at 21.29 min matches with the RT of the standard solution of SCN$^-$. The excited state molecule of 2-TBA undergoes decomposition to give SCN$^-$ as photo product.

Miura et. al. [21] have reported that the sulfur anions have high absorbance in the range of 200 – 230 nm and shown the absorbance spectra of thiocyanate anion. Chiang and Kresge [22] have
reported the change in the absorbance of the thiocyanate ion at 220 nm, measured in the concentrated aqueous perchloric acid solution.

Jochym et. al. [23] have reported the UV irradiation of the barbital yields derivative of urea and biuret and interpreted that the origin of the IR band at 2170 cm$^{-1}$ is of the isocyanate intermediate which is formed after the pyrimidine ring opening.

Table 3.8  \(\lambda_{\text{max}}\) and molar absorptivity of photoproduct and \([\text{KCNS} + \text{MB}]\) before and after exposure at 11 pH KCNS (5 x $10^{-5}$ M) and MB (2 x $10^{-5}$ M)

<table>
<thead>
<tr>
<th>Species Present</th>
<th>(\lambda_{\text{max}})</th>
<th>Molar absorptivity (L mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[KCNS + MB] Before exposure</td>
<td>225 nm</td>
<td>2472</td>
</tr>
<tr>
<td>[KCNS + MB] After exposure</td>
<td>220 nm</td>
<td>2674</td>
</tr>
<tr>
<td>Reaction product</td>
<td>220 nm</td>
<td>2540</td>
</tr>
</tbody>
</table>
The absorbance spectra of KCNS with MB before and after exposure and the reaction product

![Absorbance Spectra of KCNS with MB](image)

**Fig 3.12** The absorbance spectra of KCNS with MB before and after exposure and the reaction product

KCNS ($5 \times 10^{-5}$ M) and 2-TBA ($5 \times 10^{-5}$ M)

MB ($1.5 \times 10^{-5}$ M)

Source: 100 W tungsten lamp
Fig 3.13 IC analysis graph for std. SCN 100 ppm
Fig 3.14 IC analysis graph of photo product of 2-TBA
3.5 Discussion

2-TBA molecule has three mobile H atoms and undergoes tautomeric transformation depending upon the pH of the solution. 2-TBA has 10 tautomeric forms N1 to N10 (Fig 1). HTBA [N4 or N5 or N10] exists as dominant form out of ten tautomeric forms in acidic medium while TBA⁻ [N1] exists as dominant form out of ten tautomeric forms in alkaline medium.

The photosensitized reaction of 2-TBA and MB depends on the pH of the solution. The sensitization effect of MB is not observed between pH 2 – 6. 2-TBA exists as protonated and neutral species in equilibrium in this pH range. The protonated and neutral species of 2-TBA do not undergo photosensitized reaction.

The photosensitized reaction is observed between pH range 8 – 12. 2-TBA exists as neutral and anionic species in equilibrium in this pH range which shows $\lambda_{\text{max}}$ at 235 nm and 285 nm. The absorbance decreases with time at both the $\lambda_{\text{max}}$ on exposure of the reaction mixture to the visible light. The decrease of the absorbance is faster at 285 nm corresponding to TBA⁻ than at 235 nm for HTBA. The anionic species present in the pH range 8 – 12 undergoes photo reaction. It is suggested that the equilibrium of $\text{HTBA} \leftrightarrow \text{H}^+ + \text{TBA}^-$ is shifted to right side as the TBA⁻ decomposes.

Methylene blue molecule which is a cationic dye absorbs the visible radiation at 665 nm and is excited to singlet state which is capable of attracting electron. The anionic form of 2-TBA gets excited to singlet state by electron transfer mechanism after interaction with excited methylene blue molecule which acts as electron acceptor. However the exciplex formation is not observed.

The free radical scavenging effect of the methanol is not observed. The photochemical reaction doesn’t show change in the alkaline methanolic solvent except that the rate of the reaction slightly decreases suggests that there is no free radical formation during the reaction.

The photosensitized reaction when carried out in different organic solvent having different polarity, shows decrease in the rate of the reaction as the polarity of the solvent decreases. The electron transfer reaction between 2-TBA anion and excited state molecule of MB is more efficient in higher polar solvent while deactivation of excited 2-TBA⁻ is more efficient in non polar solvent.

The rate of the reaction determined in the anaerobic condition remains the same as in the aerobic condition suggests that no oxidation reaction takes place by the singlet state of the oxygen. Similarly the quantum efficiency value determined in the anaerobic condition shows that quantum efficiency value is the same as in the aerobic condition.
The $\phi$ value of the reaction is low ($\Phi = 0.323$); the process of the deactivation of the excited state is predominant as compared to the decomposition of the excited state of the substrate molecule. The $\phi$ value is constant with increase in the concentration of 2-TBA giving a horizontal relationship between $\phi$ value and the concentration of 2-TBA. The kinetic expression for the inverse of quantum yield based on steady state approximation and given by the equation:

$$
\frac{1}{\Phi_{\text{proc}}} = \frac{k_p + k_{ij} + k_{sd}}{k_p}
$$

Equation shows that the quantum yield of the reaction is independent of the substrate concentration. Thus, the plot of $1/\phi$ vs $1/ C$ gives a horizontal graph with zero slope indicating a singlet – singlet energy transfer mechanism between excited state MB molecule to 2-TBA anion and also suggests that there is no exciplex formation. The singlet excited state of the anionic 2-TBA molecule undergoes decomposition to give photo product [12].
3.6 Mechanism

2-TBA have it's $\lambda_{\text{max}}$ below 300 nm and does not absorb the visible light and is photo stable in the acidic and in the alkaline medium. 2-TBA undergoes electron transfer reaction with MB in the alkaline medium when exposed to the visible light. (Fig 3.15)

The experimental observation suggests that the methylene blue absorbs visible radiation and goes to the singlet excited state. Some of the singlet excited MB can deactivate to ground state by radiation deactivation. The singlet excited state of MB molecule transfers energy to TBA$^{-}$ molecule by electron transfer mechanism and the TBA$^{-}$ molecule goes to the singlet excited state. Deactivation of some of the singlet excited TBA$^{-}$ molecule to ground state occurs because the $\varphi$ value of the reaction is low.

The plot of $1/\varphi$ Vs $1/C$ is horizontal with zero slope suggests that energy transfer from singlet excited state of methylene blue molecule to 2-TBA anion takes place. Singlet excited cationic MB molecule acts as electron acceptor and singlet – singlet energy transfer excites the 2-TBA anion to singlet excited state which undergoes decomposition.

The excited TBA$^{-}$ molecule undergoes decomposition by reorganisation to give SCN$^{-}$ as a photo product. The photo product SCN$^{-}$ is an anion which appears to undergo an electron transfer reaction with the excited molecule of MB. The electron transfer from SCN$^{-}$ to MB result in the formation of an [SCN$^{-}$ MB$^+$] exciplex which shows increased absorbance and hypsocromic shift in comparison to the solution of the same concentration of SCN$^{-}$ and MB in the ground state. (Fig 3.11)

The reaction of 2-TBA takes place in the presence of the cationic dye MB on irradiation with visible light at pH 10. 2-TBA exists in equilibrium as protonated and anionic form at pH 10. The irradiation of MB molecule with visible light excites it to singlet excited state which interacts with anionic form of 2-TBA which is excited to singlet state. The excited 2-TBA anion undergoes decomposition and gives SCN$^{-}$ as photo product.

The rate of the photo decomposition reaction of 2-TBA is independent of the concentration of 2-TBA and MB but dependent on the pH of the solution and light intensity. The energy transfer from excited molecule of MB to 2-TBA is dependent on the polarity of the solvent. The plot of $1/\varphi$ Vs $1/C$ suggests singlet – singlet energy transfer from the sensitizer molecule to substrate anion molecule without exciplex formation. The photo product is formed by the decomposition of the singlet excited state of 2-TBA anion.
Mechanism of 2-TBA Degradation

\[ [MB^+] \xrightarrow{hv} [MB^+]^{*1} \quad \text{Irradiation} \quad (1) \]

\[ [MB^+]^{*1} \longrightarrow [MB^+] + \text{heat} \quad \text{Deactivation} \quad (2) \]

\[ [MB^+]^{*1} + [TBA^-] \longrightarrow [MB^+] + [TBA^-]^* \quad \text{Energy Transfer by Electron Transfer} \quad (3) \]

\[ [TBA^-]^* \longrightarrow [TBA^-] \quad \text{Deactivation} \quad (4) \]

\[ [TBA^-]^* + [TBA^-] \longrightarrow 2\text{-TBA} \quad \text{Concentration Quenching} \quad (5) \]

\[ [TBA^-]^* \longrightarrow [SCN^-] \quad \text{Decomposition by Reorganization} \quad (6) \]

\[ [SCN^-] + [MB^+]^{*1} \longrightarrow [SCN^\cdot MB^+] \quad \text{Electron Transfer Exciplex Formation} \quad (7) \]

Fig 3.15 Mechanism of 2-TBA Degradation
3.8 References


