Photosensitized Reaction of Quinaldine: Kinetics and Mechanism

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Abstract: The photosensitized reaction of Quinaldine (2-methyl-8-hydroxyquinoline) has been studied in the alkaline medium in the visible light using Methylene blue (MB) as photo sensitizer. The rate of the reaction has been calculated. The effect of the parameters like pH, concentration of the sensitizer, concentration of the substrate, and intensity of the light on the rate of the photosensitized reaction has been studied. The reaction has been studied in anaerobic condition to observe the effect of the oxygen. Methanol shows free radical scavenging effect. The quantum efficiency of the photosensitized reaction has been calculated. The scheme of the reaction mechanism is suggested. The singlet state of the oxygen (\(^1\)O\(_2\)) participates in the photoreaction and photo oxidation products are formed by oxidation of the substrates. The reaction has been studied using U.V.-visible spectroscopy and product analyzed with Mass-Spectrometry.

Keywords: Photosensitized Reaction, Methylene Blue, 2-Methyl-8-Hydroxyquinoline (Quinaldine), Rate of Reaction.

1. Introduction

The 2-Methyl-8-Hydroxyquinoline (Quinaldine, 2-M-8HQ) is used as an anti-malarial and for preparing other anti-malaria drugs [1]. The strong N-H - O hydrogen bond suggest the occurrence of the proton transfer reaction proceeding without a considerable barrier. Bardez et al.[2] have reported that the intramolecular proton transfer between the OH group and the N atom of the ring may take place. Theoretical studies of 8-HQ tautomerization were carried out by Li and Fang [3]. There is some suggestion that the tautomeric equilibrium undergoes the action of medium; e.g., aqueous solutions of 8-HQ contain as little as 2% of its zwitterionic tautomer [4]. 8-Hydroxyquinoline (8-HQ) exists predominantly as a neutral molecule in the solid state it exists as a zwitter ion in aqueous solutions, the coexistence of a tautomeric form is in equilibrium with the neutral enolic form [5].

The direct oxidation of 8-Hydroxyquinoline has been reported by Bock H et al [6] using sodium nitrite and gives quinoline-5, 8-quinone in very low yield. The kinetics of the thermal oxidation of 8-Hydroxyquinoline is reported by A.N. Palaniappan et al.[7]. Ananda S. Amarasakara has reported the dye-sensitized photo oxidation reaction of 8-Hydroxyquinoline or 5-Hydroxyquinoline [8] and Janine Cossy & Damien Belotti have studied the dye sensitized photooxidation of Quinaldine and their derivatives [9] which obtained 2-methyl-quinoline-5,8-quinone as photoproduction in dichlororomethane and methanolic solution and oxidized photoproduc and the structure of the product was conformed using Mass-spectrometry,\(^1\)H NMR and \(^{13}\)C NMR methods. A number of reagents or methods suitable for the preparation of substituted quinoline-5,8-quinones has been develop[11-14]. Among these, the most widely used oxidizing agent for the transformation of substituted 8-hydroxyquinolines to substituted quinoline-5,8-quinones is Fremy’s salt [15].

The present study reports the study of photosensitized reaction of 2-methyl-8-hydroxyquinoline with the cationic dye methylene blue (MB) as a photosensitizer which has also been used as sensitizer in a number of photochemical reactions [16-20]. MB shows two different type of energy transfer process. (a) Electron transfer reactions including exciplex formation. (b) Energy transfer to triplet O\(_2\) to convert it to singlet oxygen for photooxidation.

Several molecular complexes have been reported in the literature by electron transfer process between methylene blue and different compounds [21-23]. The Photo oxygenation of 8-HQ, 2-M-8HQ and some of their derivatives has been studied by Janine Cossy and Damien Belotti [9] and quinoline-5, 8-quinone was obtained as oxidized photoproduc and the structure of the product was conformed using Mass-spectrometry,\(^1\)H NMR and \(^{13}\)C NMR methods. A number of reagents or methods suitable for the preparation of substituted quinoline-5,8-quinones has been develop[24-27]. Among these, the most widely used oxidizing agent for the transformation of substituted 8-hydroxyquinolines to substituted quinoline-5,8-quinones is Fremy’s salt [28]. A number of studies have been reported on the photosensitization processes of methylene blue in the presence of the oxygen. Tanielian et al. [29] have reported the kinetic and mechanism study of the photosensitization by methylene blue in the presence of the oxygen. Silva et al. [30] have reported photosensitization and oxidation of Lysozyme in the presence of methylene blue. Methylene blue Photosensitized hydroxylation and oxidation with singlet oxygen have been reported in the literature [31-35]. Generation of singlet molecular oxygen by
photosensitization with methylene blue (MB) supported in Nafion-Na films has been reported by Wetzler DE et al. [36]. Methylene blue photosensitized oxidation of encephalin in the presence of nitrite has been reported by Fontana et al. [37]. Photodynamic effect of MB under aerobic and anaerobic conditions has been reported by McCullagh C et al. [38].

2. Materials and Methods

2.1 Materials

All the chemicals are of analytical grade and used as received. Stock solutions were prepared in doubly distilled water.

2.2 Experimental Part

The photosensitized reaction of the Quinaldine in the presence of methylene blue in the alkaline medium has been studied in the visible light using a 100W tungsten lamp for the irradiation. The photosensitized reaction has been isolated and identified. The singlet state of the oxygen (\( ^1O_2 \)) participates in the photo reaction and photo oxidation product is formed by oxidation of the substrates. Quinaldine with methylene blue does not form photoproduct without irradiation. The rate of the reaction has been calculated by measuring the change of the absorbance at the \( \lambda \)-max of the Quinaldine with time. The effects of the different parameters e.g. pH, concentration of the sensitizer, concentration of the substrate, the intensity of the light on the rate of the photosensitized reaction have been studied and the reaction conditions have been established. The rate of the reaction has also been studied in the anaerobic condition to observe the role of the oxygen in the reaction.

The quantum efficiency of the photosensitized reaction has been evaluated using potassium ferrioxalate actinometer. The effect of the substrate concentration on the quantum efficiency has been studied to evaluate the different excited state of the substrate molecule. The quantum efficiency has also been studied in the anaerobic condition. The photoproduct has been isolated, purified and analyzed with mass spectrometry. The mass spectrum of the product has been compared with the reported mass spectrum. The mechanism of the photosensitized reaction has been suggested.

3. Results and Discussion

3.1 Results

3.1.1 Spectral Characteristics

The spectrum of the pure Quinaldine was recorded in the pH range 2-12 in the range of 200-400nm. The spectrum of the pure Quinaldine was recorded in the acidic medium. The pH of the solutions was maintained using suitable concentration of HCl. The –OH group gets protonated to –OH\(^+\) up to pH 3 and shows \( \lambda \)-max of cationic form of Quinaldine show \( \lambda \)-max at 254 nm & 310 nm-315 nm corresponding to \( \pi-\pi^* \) and n-\( \pi^* \) transition respectively. The spectrum of the pure quinaldine was recorded in the pH range 4-8 and \( \lambda \)-max of neutral form are observed at 240nm & 285nm and for \( \pi-\pi^* \) and n-\( \pi^* \) respectively. The spectrum of pure quinaldine was recorded in the pH range 9-12. The pH of the solution was maintained using suitable concentration of NaOH. The –OH group gets deprotonated to –O in the pH above 8. The absorbance bands corresponding to \( \pi - \pi^* \) and n-\( \pi^* \) transition for quinaldine at 255nm & 330-340 nm respectively. Spectra of quinaldine was recorded in the spectral range of 200-400nm under experimental conditions against reagent blank.

The spectrum of the pure quinaldine shows that compound exist in different form in the acidic, neutral and alkaline medium correspond different \( \lambda \)-max at the different pH (Table-1). Reported \( \lambda \)-max, molar absorptivity of quinaldine with different pH (Table-2) and measured \( \lambda \)-max & molar absorptivity are shown the spectrum of reaction mixture containing quinaldine and methylene blue were recorded without exposing to the visible radiation and after exposure to the visible radiation in the pH range between 2 to 12. The spectrum of the reaction mixture was recorded after keeping the solution in dark for 24 hours against reagent blank. The spectrum of the reaction mixture remains same as the solution of the substrate without exposing to the visible radiation. quinaldine and methylene blue does not show reaction in the ground state.

The spectrum of the reaction mixture of quinaldine and MB were recorded after exposure to the visible radiation in the pH range 2-12 against a reagent blank. The spectra shows change in the absorption pattern with time. quinaldine show reaction on exposure to the visible radiation in the presence of MB. The quinaldine exist in cationic (protonated) form at pH lower than 3 and it exist in the neutral form between pH 4 to 8 while it exist in anionic (deprotonated) form between pH 9-12 (Fig.-1). The photosensitized reaction of quinaldine (2M-8-HQ) studied at pH 4 to 12 (Fig.-2). Absorption band at 255nm (of 2M-8-HQ) show decrease in the intensity and a new absorption band appears at 225nm and 270nm for 2M-8-HQ as the photoreaction product formation takes place.

3.1.2 Product Study

The mass spectrum of the photoprodut of the 2M-8-HQ in aqueous alkaline solution has been evaluated and compared with the reported mass spectrum and mass fragmentation of the 2-Methyl-Quinoline-5, 8-quinone expected sample under experimental condition. The reaction product was isolated by extracting exposed solution 4 times with 5ml Dichloromethane (DCM) solvent. Dichloromethane (DCM) solvent was collected and evaporated to dryness and product was dissolved in 5 ml methanol. The methanolic solution of the product was used for mass spectrometric analysis.

3.1.3 The rate of the reaction

The reaction mixture containing substrate and sensitizer at pH 11 was exposed to the visible light. Absorption band for 2M-8HQ at 255nm decrease and the absorbance bands at
The increase of light intensity [Einstein / second] (E/s) shows positive effect and rate of the photochemical reaction increases as the light intensity increases. The number of excited molecules of the sensitizer increases with higher light intensity and correspondingly the rate of reaction also increases (Table-4). A linear relationship is observed between the light intensity and the rate of the reaction. The half-time reaction is calculated at different initial concentration of the substrate and $t_{1/2}$ value is constant over the above range of the concentration. The photochemical reaction is of the first order.

3.2.5 The Effect of the anaerobic condition

Study was carried out to see the effect of oxygen concentration on the rate of the reaction. A purified nitrogen gas was passed through the solution of 2M-8-HQ and MB for 20 minutes to remove dissolved oxygen of the solution. Maximum deoxygenated reaction mixture of the 2M-8HQ and MB was exposed to the visible light. The rate of the reaction was calculated. It decreases in the anaerobic condition (Table-5). Quantum yield of the photosensitized reaction was calculated and it shows decrease in the anaerobic condition (Table-6). MB gets excited to singlet state upon irradiation. Excited singlet state of MB undergoes inter system crossing (ISC) and forms triplet state which transfers energy to the triplet state of the oxygen to form singlet state oxygen. The singlet state oxygen is a good oxidizing agent. Photoreaction is dependent on singlet state of the $O_2$ which suggests that oxygen participates in the photosensitized reaction of the 2M-8HQ. Concentration of singlet oxygen ($^1O_2$) decreases in anaerobic condition. Therefore the oxidation decreases due to small concentration of the singlet state oxygen. Photochemistry of 2-Methyl-8-Hydroxyquinoline has been reported by Janine Cossey and Damien Belotti [9] in the presence and the absence of oxygen, in methylene chloride solution. The formation of the singlet state oxygen in different solvent and the different sensitizer study has also been reported [39,40].

3.2.6 The Effect of the solvent

The effect of the solvent on photosensitized reaction of the 2M-8HQ was studied by changing the medium from aqueous alkaline to methanolic alkaline. The 2M-8-HQ show absorbance bands of $\pi - \pi^*$ and $n - \pi^*$ transitions at 255 nm & 330-340nm respectively in the alkaline methanol. The rate of the reaction slightly decreases in 2-M-8-HQ but reaction takes place as in the aqueous solution. The free radical scavenging effect in methanolic solution is not observed. The photoreaction of 2-M-8-HQ does not proceed via a free radical intermediate formation in methanolic solution and rate of the reaction calculated (Table-7).

3.2.7 The quantum efficiency $[(\phi) Value]$

The quantum efficiency of the photochemical reaction was determined by using potassium ferrioxalate as an actinometer at different initial concentration of the substrates (Table-9). It was also determined in the anaerobic condition (Table-8). The plot of the $\phi$ value and the initial concentration of the substrate show a horizontal relationship with zero slope [41]which suggest that the $\phi$ value of the photochemical reaction is independent of the initial concentration of the substrate. The energy transfer takes place from the singlet excited state of the sensitizer molecule to the substrate molecule.

The plot of the inverse of the quantum efficiency versus inverse of the concentration of the substrate is horizontal with zero slope [41]. The quantum efficiency of the anaerobic reaction is approximately ten times lower than quantum efficiency of aerobic reaction. It shows that the photosensitized reaction is less efficient in anaerobic condition.
The photosensitized reaction of 2-M-8-HQ does not show any change in the reaction pattern except slight decrease in the rate of the reaction which carried out in methanolic solution. The rate of the reaction is dependent on pH, light intensity but is independent of initial concentration of the substrate, sensitizer concentration and concentration of molecular oxygen (\(1O_2\)). The 2-M-8-HQ existence is in equilibrium in neutral and anionic form. The anionic form of quinaldine (2M-8HQ) does not show free radical formation observed in methanolic solution of 2-Methyl-8-Hydroxyquinoline suggesting does not free radical formation. The rate of the reaction which carried out in methanolic solution of 2-M-8-HQ to give the photoprodct. Reaction of 2M-8HQ with the singlet state of MB is affected by the absence of \(1O_2\) so, the experimental observation of rate of the reaction and quantum efficiency of the reaction in anaerobic condition suggests that product formation involve oxidation by singlet state of the oxygen (\(1O_2\)). Methylene blue is excited to the singlet excited state on exposure to the visible radiation. MB absorbs visible radiation and is excited to the singlet excited state of MB which transfers its energy to 2M-8-HQ which undergo photosensitized chemical reaction. The anionic form of 2M-8HQ shows absorption band at 255 nm which decrease in intensity and a new absorption bands appear at 225 nm and 270 nm on exposure to the visible light in the presence of MB.

### 3.4. Mechanism

![Mechanism Diagram](image)

### 4. Conclusion

The anionic form of quinaldine (2M-8HQ) does not show spectral changes on the exposure to the visible light of photosensitized reaction. The 2M-8HQ existence is equilibria in neutral and anionic form. The anionic form of 2M-8HQ photosensitized oxidation reaction in presence of methylene blue in the alkaline medium. Spectral profile of the exposed solution suggests that photo product of reaction is 2-methyl-quinoline-5, 8-quinone. The photoreaction is observed in methanolic solution of 2-Methyl-8-Hydroxyquinoline suggesting does not free radical formation occurs. The photoreaction does not take place in the anaerobic condition suggests the singlet oxygen participate in the reaction. The rate of the reaction is dependent on pH, light intensity but is independent of initial concentration of the substrate, sensitizer concentration and concentration of oxygen.

### 5. Acknowledgements

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### References


Author Profile
Krupa Jani completed the B.Sc. and M.Sc. degrees in Chemistry from Gujarat University. PhD in Chemistry Specializations subject is Photochemistry during 2006-2013 from Gujarat University. Recently work with the Government Science College, Gandhinagar as Assistant Professor.

Figures

Figure 1: Spectrum of Quinaldine at different pH with different form
Substrate: [2M-8HQ] = 2.0 x 10⁻⁵ M

Sensitizer : [MB] = 2.0 x 10⁻⁶ M

Light intensity = 11.18 E/S
pH = 11

Table 1: Effect of pH on π - π* and n - π* transition and Molar absorptivity of quinaldine

<table>
<thead>
<tr>
<th>Form</th>
<th>pH</th>
<th>π - π* Experimental ε value</th>
<th>n - π* Experimental ε value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>2 pH</td>
<td>254 nm</td>
<td>32,800</td>
</tr>
<tr>
<td>Neutral</td>
<td>4-8 pH</td>
<td>240 nm</td>
<td>33,600</td>
</tr>
<tr>
<td>Anion</td>
<td>9-12 pH</td>
<td>255 nm</td>
<td>31,400</td>
</tr>
</tbody>
</table>

Table 2: Reported λ-max and molar absorptivity of quinaldine

<table>
<thead>
<tr>
<th>Form</th>
<th>pH</th>
<th>λ-max nm</th>
<th>Reported ε value</th>
<th>n - π* Reported ε value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>4-8 pH</td>
<td>242 nm</td>
<td>33,450</td>
<td>283 nm</td>
</tr>
</tbody>
</table>

Table 3: Rate of the reaction of 2-methyl-8-HydroxyQuinoline

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate of the reaction (K) x 10⁻³ mol L⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Substrate: [2M-8HQ] = 2.0 x 10⁻⁵ M

Table 4: Effect of the light intensity on the rate of the reaction of 2M-8HQ

<table>
<thead>
<tr>
<th>Intensity of light I x 10⁸ E/S</th>
<th>Rate of the reaction (K) x 10⁻³ mol L⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Substrate: [2M-8HQ] = 2.0 x 10⁻⁵ M

Table 5: Effect of anaerobic condition on the rate of the reaction of 2M-8HQ: (Study of the role of singlet oxygen)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate of the reaction (K) x 10⁻³ mol L⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Table 6: Effect of anaerobic condition on the Quantum efficiency of 2M-8HQ

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantum efficiency (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>0.265</td>
</tr>
</tbody>
</table>

Substrate: [2M-8HQ] = 2.0 x 10⁻⁵ M

Table 7: Effect of solvent on the rate of the reaction of 2M-8HQ: (Study of the free radical scavenging effect of methanol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate of the reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Table 8: Quantum efficiencies of 2-Methyl8-HydroxyQuinoline Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Φ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>0.265</td>
</tr>
</tbody>
</table>

Table 9: The photoproduct of 2-Methyl- 8-Hydroxyquinoline

<table>
<thead>
<tr>
<th>Compound</th>
<th>The photoproduct of 2-Methyl- 8-Hydroxyquinoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M-8HQ</td>
<td>C₁₀H₈NO₂ C₉H₄NO₂ C₉H₉N⁺ C₇H₅N⁺ C₆H₄⁺ C₃HN⁺</td>
</tr>
</tbody>
</table>

M/Z Value

<table>
<thead>
<tr>
<th>Fragment ions</th>
<th>M/Z Value</th>
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</thead>
<tbody>
<tr>
<td>C₁₀H₈NO₂</td>
<td>174.0</td>
</tr>
<tr>
<td>C₉H₄NO₂</td>
<td>158.0</td>
</tr>
<tr>
<td>C₉H₉N⁺</td>
<td>131.0</td>
</tr>
<tr>
<td>C₇H₅N⁺</td>
<td>103.0</td>
</tr>
<tr>
<td>C₆H₄⁺</td>
<td>76.0</td>
</tr>
<tr>
<td>C₃HN⁺</td>
<td>51.0</td>
</tr>
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