Kinetics and mechanism of quinaldine with methylene blue as photo sensitizer

Krupa P. Jani

Government Science College, Sector-15, Gandhinagar, Gujarat, India
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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 ($^1O_2$) 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.
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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 euillibrium 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. Amarasekara 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 photoproduct in dichloromethane and methanolic solution and oxidized photoproduct and the structure of the product was conformed using Mass-spectrometry,^{1}H NMR and ^{13}C NMR methods. The kinetics of the rose bengal (RB) sensitized photo oxidation of 8-Hydroxyquinoline in pH 6 aqueous solution and in organic media is reported by A. Pajares and S. Criado et al.[10], and have concluded that 8-OHQ is effectively photooxidised with $O_2(^1Dg)$, faster if the OH group is ionised.

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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-8-HQ and some of their derivatives has been studied by Janine Cossy and Damien Belotti [9] and quinoline-5, 8-quinone was obtained as oxidized photoproduct 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 have 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].

MATERIALS AND METHODS

Materials: All the chemicals are of analytical grade and used as received. Stock solutions were prepared in doubly distilled water.
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 photoproduct 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 λ-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 on 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.

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RESULTS AND DISCUSSION

Spectral Characteristics:
The spectrum of the pure Quinaldine was recorded in the pH rang 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 $-OH_2^+$ up to pH 3 and shows λ-max of cationic form of Quinaldine show λ-max at 254 nm & 310 nm-315 nm corresponding to π-π* and n-π* transition respectively. The spectrum of the pure quinaldine was recorded in the pH range 4-8 and λ-max of neutral form are observed at 240nm & 285nm and for π-π* and n-π* 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 π - π* and n-π* 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.

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

Form	pH	π - π *	Experimental ε value	n - π *	Experimental ε value
Cation	2 pH	254 nm	32,800	310-315 nm	1520-1630
Neutral	4-8 pH	240 nm	33,600	285 nm	2950
Anion	9-12pH	255 nm	31,400	330-340 nm	2960-2990

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

Form	pH	π - π *	Reported ε value	n - π *	Reported ε value
Neutral	4-8 pH	242 nm	33,450	283nm	2900

Table-3. Rate of the reaction of 2-methyl-8-HydroxyQunoline

Compound	Rate of the reaction (K) $\times 10^{-3}$ mol $L^{-1}min^{-1}$
2M-8HQ	42.5
Substrate:[2M-8HQ] = 2. 0$\times 10^{-5}$ M Sensitizer:[MB] = 2. 0$\times 10^{-6}$ M Light intensity = 11. 18 E/S pH = 11	

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

Intensity of light I $\times 10^8$ E/S	Rate of the reaction (K) $\times 10^{-3}$ mol $L^{-1}min^{-1}$
	2M-8HQ
4. 85	14.5
6. 87	23.0
11. 18	42.5

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

Compound	Rate of the reaction (K) $\times 10^{-3}$ mol L^{-1} min^{-1}	
	Aerobic condition	Anaerobic condition
2M-8HQ	42.5	0. 82

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

Compound	Rate of the reaction (K) $\times 10^{-3}$ mol $L^{-1}min^{-1}$	
	Aqueous alkaline solution	Methanolic alkaline solution
2M-8HQ	42.5	39.7

Table-8. Quantum efficiencies of 2-Methyl8-HydroxyQuinoline & Derivatives

Compound	2M-8HQ
Φ value	0.265

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

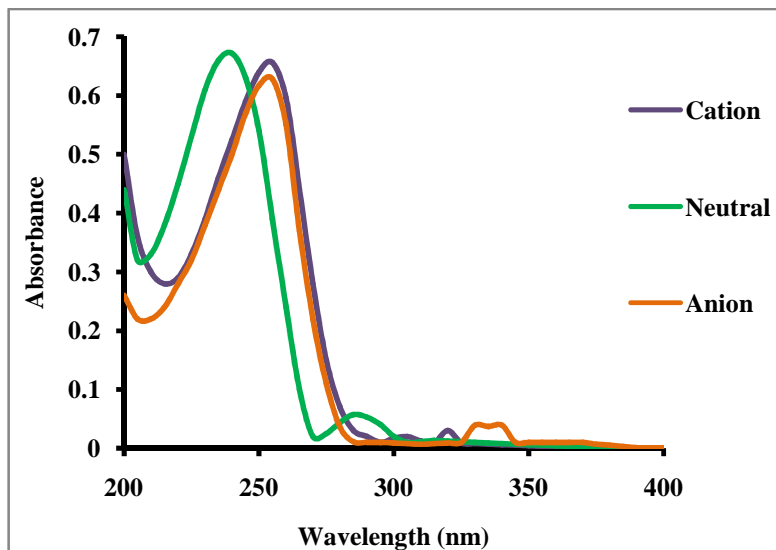| Fragment ions	$C_{10}H_8NO_2$	$C_9H_4NO_2^+$	$C_9H_9N^+$	$C_7H_5N^+$	$C_6H_4^+$	C_3HN^+
M/Z Value	174.0	158.0	131.0	103.0	76.0	51.0

Fig.-1. Spectrum of Quinaldine at different pH with different form
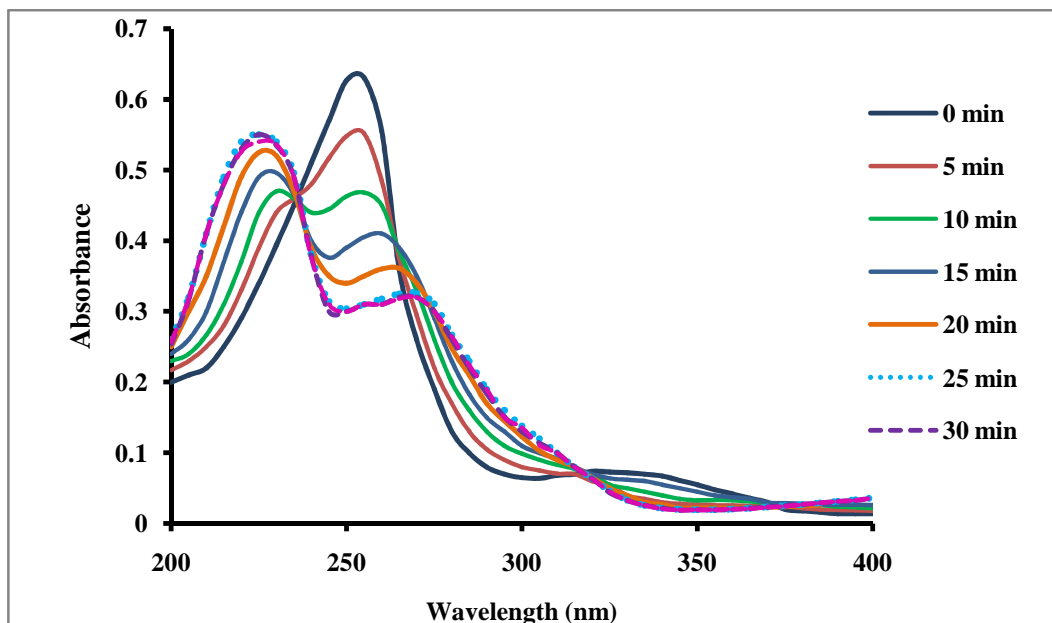*Substrate : [2M-8HQ] = 2.0 x 10^{-5} M*

Fig-2. Spectrum of Quinaldine and MB on exposure with time
Substrate : [2-M-8-HQ]= 2.0 x 10^{-5} M
Sensitizer : [MB]= 2.0 x 10^{-6} M
Light intensity= 11.18 E/S
pH = 11

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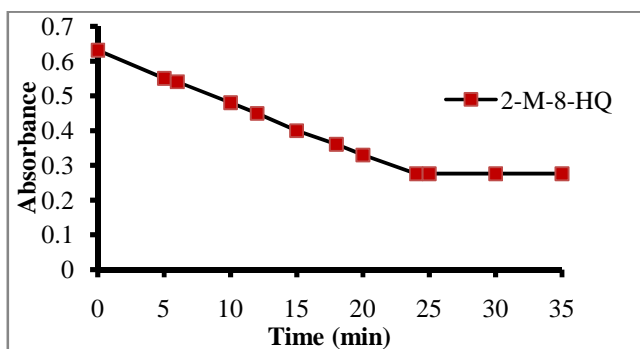
Fig.-8. Absorbance of 2M-8HQ and MB on exposure with Time at λ max of 2M-8HQ
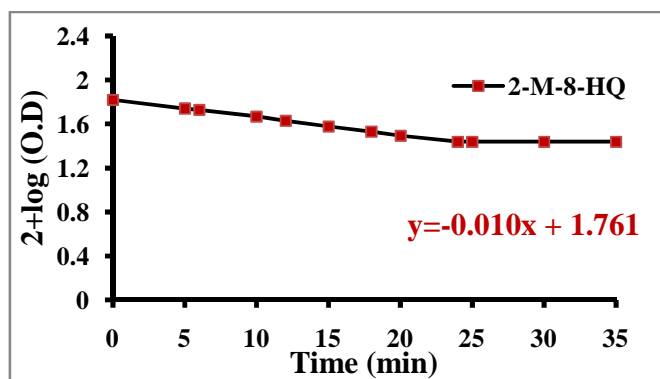

y=-0.010x + 1.761

Fig.-9. 2+log(O.D.) of 2M-8HQ and MB on exposure with Time at λ max of 2M-8HQ
Substrate:[2M-8HQ] = 2. 0×10⁻⁵ M
λmax : 2-M-8-HQ = 255nm
Sensitizer:[MB]   =   2. 0×10⁻⁶ M
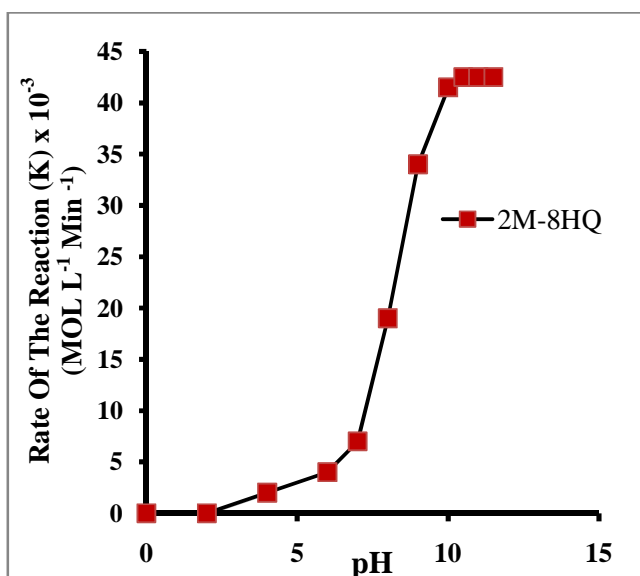*Light intensity   =   11. 18 E/S*
pH   =   11

Fig-10: Graph of rate of the reaction of 2M-8-HQ at different pH
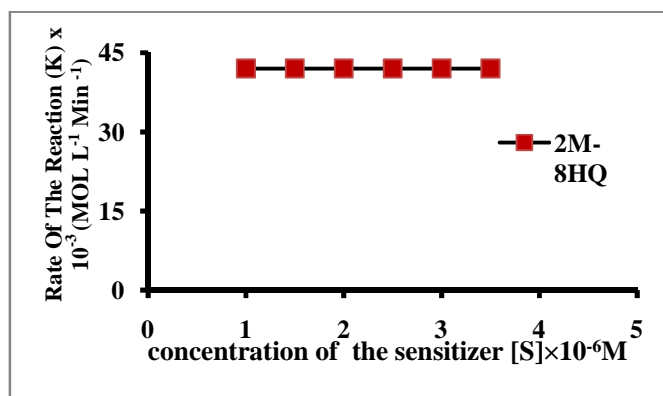
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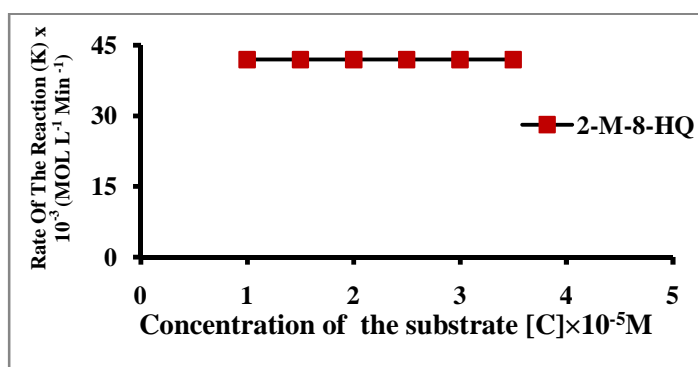**Fig-11: Effect of the sensitizer concentration on the rate of the reaction**

Fig-12: Effect of the substrate concentration on the rate of the reaction
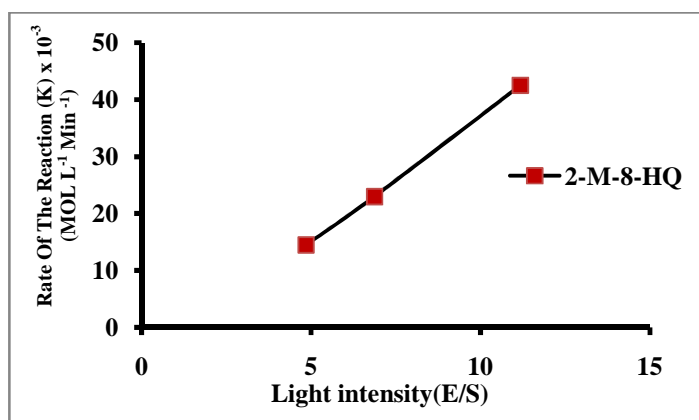

Fig-13: Graph of effect of the Light intensity (E/S) on the rate of the reaction

The Spectrum of the pure quinaldine shows that compound exist in different form in the acidic, neutral and alkaline medium correspond different λ-max at the different pH (Table-1). Reported λ-max, molar absorptivity of quinaldine with different pH (Table-2) and measured λ-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 were 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.

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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.

Product study:
The mass spectrum of the photoproduct 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.

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 decreases and the absorbance bands at 220nm and 270nm increases corresponding to the photoproduct. The decrease of the absorbance at 255nm of 2M-8HQ has been measured at different time intervals; which becomes constant after 30.0 min indicating the completion of the reaction (Fig.-3). The result of a typical run for quinaldine (2M-8HQ) have been presented (Fig.-4). The decrease of the absorption for 2M-8HQ at 255nm have been used to calculate the rate constant for reaction. The rate of the photosensitized reaction for 2-Methyl-8-Hydroxyquinoline have been calculated (Table-3). A plot of 2 + log (O.D.) with time was prepared and slope was determined (Fig.-4). The rate constant was calculated by following formula.

Rate constant = 2. 303 x Slope

The photosensitized reaction shows different rate for 2M-8-HQ in experimental conditions (Table-3).
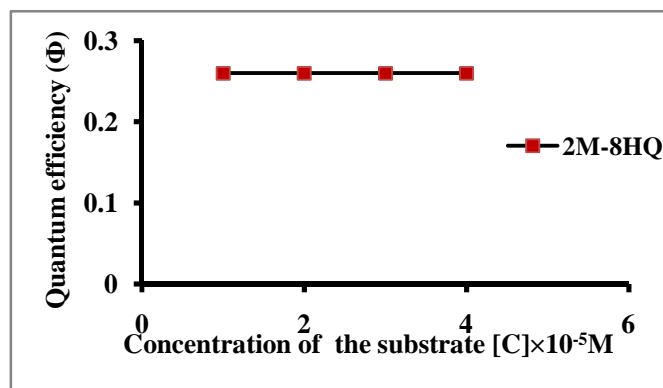

Fig-14. Effect of the substrate concentration on the quantum efficiency

THE EFFECT OF VARIABLES ON THE RATE OF THE REACTION
The Effect of the pH:
The photosensitizer effect of methylene blue on 2M-8HQ has not been observed in the acidic medium up to pH 3 but the reaction is observed when pH becomes 4 and rate constant of the photosensitized reaction has been calculated for 2M-8HQ with pH range 4-12. The reaction rate increases in this pH range and becomes constant at pH 11. The pH of the solution was maintained at 11 in the subsequent studies. (Fig.-5)

The Effect of the concentration of the Sensitizer:
The effect of different concentration of methylene blue on the rate of photosensitized reaction was studied. The rate constant was determined for 2M-8-HQ taking MB in the concentration range of 1 x 10^{-6} M – 3.5 x 10^{-6} M. The rate of the reaction remains constant for this concentration range of the sensitizer. The rate of the reaction slightly

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decreases at higher concentration of the sensitizer, which may be due to higher deactivation effect of the sensitizer at the higher concentration (Fig.-6).

The Effect of the concentration of the Substrate:
The effect of different initial concentration of 2-M-8-HQ on the rate of the reaction was studied in the concentration range of 1×10^{-5} M – 3.5×10^{-5} M. Rate of the reaction remains constant in this concentration range of the substrate. Rate of the reaction is independent of the initial concentration of the substrate (Fig.-7).

The Effect of the light intensity:
The increase of light intensity [Einstein / second] (E/s) shows positive effect and rate of the photo-chemical 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 (Fig.-8).

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.

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-8HQ 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 Cossy 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].

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. 2M-8-HQ show absorbance bands of $\pi - \pi *$ and $n - \pi *$ transition 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).

The quantum efficiency [(ϕ) 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 ϕ value and the initial concentration of the substrate show a horizontal relationship with zero slope [41]which suggest that the ϕ 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 (Fig.-9).

The plot of the inverse of the quantum efficiency versus inverse of the concentration of the substrate is horizontal with zero slope [41] (Fig.-10). 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 and concentration of the oxygen plays an important role in the product formation.
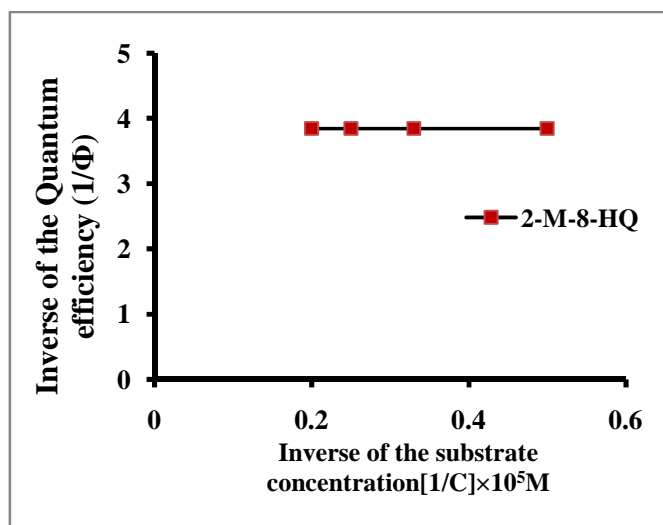

Fig-15. Plot of inverse of the substrate concentration (1/[c]) versus inverse of the quantum efficiency (1/[Φ])

DISCUSSION

The solution of the 2M-8-HQ at different pH between 2 to 12 does not absorb visible radiation and spectral changes on the exposure to the visible light are not observed.

Spectrum of the exposed reaction mixture up to pH 3 remains the same as the control solution suggesting that the cationic form of 2M-8-HQ do not undergo photosensitized reaction. 2M-8HQ with methylene blue at pH between 4 to12 show spectral changes with time when exposed to the visible light. This suggests that a photochemical reaction occurs in the neutral and the anionic form of the 2M-8HQ in the presence of sensitizer MB. The 2M-8-HQ in the pH range 4-12 of the neutral and the anionic form are in equilibrium. Cationic dye MB absorbs visible radiation and is excited to the singlet state which transfers its energy to 2M-8-HQ which undergo photochemical reaction. Plot of the quantum efficiency versus concentration ($\Phi \rightarrow C$) shows a horizontal relationship, which suggest singlet state energy transfer from singlet excited state sensitizer molecule to the substrate molecule [41]. Plot of the inverse of the quantum efficiency versus inverse of the concentration of substrate ($1/\Phi \rightarrow 1/C$) is a horizontal line with zero slope, suggests that exciplex formation does not take place between the excited state of cationic dye MB and2M-8HQ on exposure to the visible light. The anionic form of 2M-8HQ show absorption band at 255 nm which decrease in intensity and a new absorption band appear at 225 nm and 270nm on exposure to the visible light in the presence of MB.
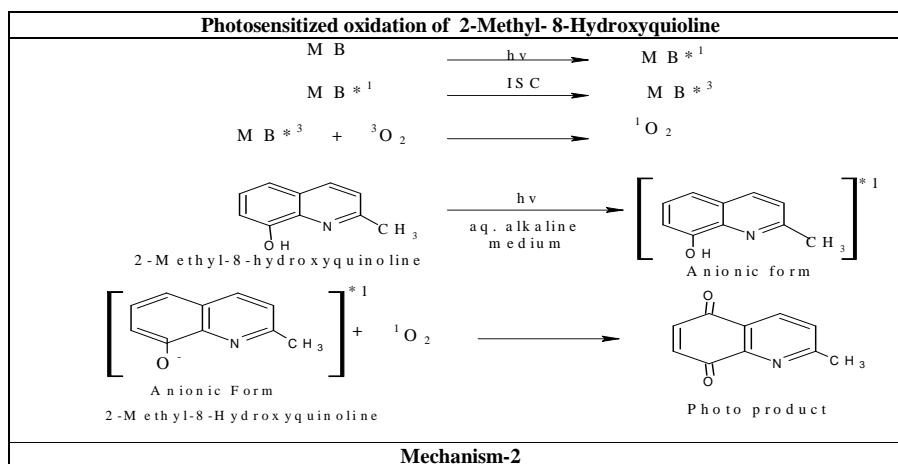
The photosensitized reaction of 2-M-8-HQ does not show any change in the reaction pattern except slight decrease in the rate of the reaction which carried out in methanolic solution. The reaction does not take place via formation of a free radical. There was no interaction between MB and 2M-8HQ without exposure to the visible radiation. The rates of the reaction calculate for 2-M-8-HQ methanolic alkaline solution which are compare to aqueous alkaline solution of 2-M-8-HQ. Reaction of the 2M-8HQ with MB in the aerobic and anaerobic condition in alkaline medium on exposure of visible light the spectral changes with remains unchanged, suggesting that, the photoproduct formation of 2M-8HQ with excited state of MB is affected by the absence of O_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. The singlet excited state of MB undergoes ISC and forms triplet excited state- which transfers the energy to triplet state of the oxygen to form singlet state oxygen. Singlet state oxygen oxidizes singlet excited anionic form of 2M-8-HQ to give the

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photoproduct. Reaction of 2M-8HQ with the singlet molecular oxygen ($^1O_2$) in the mixture containing methylene chloride and methanol has been reported by A.S.Amarasekara [8].

Mass spectroscopy data of the 2M-8HQ compared with the reported mass data of the 2-Methyl-Quinoline-5, 8-quinone the photoproduct, which suggest that 2-Methyl-quinoline-5, 8-quinone for 2-M-8-HQ are the only photoproduct. The photoreaction product of the 2M-8HQ and MB were isolated, purified and analyzed. The m/z values of photoproduct are listed in table-9.

MECHANISM:

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 equilibriums 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.

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