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PHOTOSENSITIZED REACTION OF 8-HYDROXY QUINOLENE

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ABSTRACT

The photosensitized reaction of 8-Hydroxyquinoline have been studied in the alkaline medium in the visible light using methylene blue (MB) as photosensitizer. The rate of the reaction have 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 have 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 have been calculated. The scheme of the reaction mechanism is suggested. The singlet state of the oxygen ($^1O_2$) participates in the photoreaction and photooxidation product is formed by oxidation of the substrate. The reaction have been studied using UV-visible spectroscopy and product analyzed with Mass-Spectrometry.

Key words: Photosensitized reaction, Methylene blue, 8-Hydroxyquinoline, Rate of reaction.

INTRODUCTION

8-hydroxyquinoline is a heterocyclic aromatic organic compound having molecular formula of C_9H_7NO. The strong N…H-O hydrogen bond suggests the occurrence of the proton transfer reaction proceeding without a considerable barrier. Bardez et al.[1] 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[2]. 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[3]. 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[4].

Quinoline and its derivatives are widely used in making drugs, fungicides, biocides, antibacterial, rubber chemicals and flavoring agents[5,6]. 8-Hydroxyquinoline and their derivatives show cytotoxic effect[7,8]. It is used in preparing antiseptics, deodorants, antiperspirants, and preservatives[9-13]. The 8-hydroxyquinoline and its derivatives are widely used as chelating reagents in analytical chemistry and radiochemistry for metal ion extraction and fluorometric determination[14].

The direct oxidation of 8-hydroxyquinoline has been reported by Bock et al.[15] 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 Palaniappan et al.[16]

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Amarasekara[17] has reported the dye sensitized photo oxidation reaction of 8-Hydroxyquinoline or 5-Hydroxyquinoline and Cossy and Belotti[18] have studied the dye sensitized photooxidation of 8-hydroxyquinoline and their derivatives, which obtained quinoline-5,8-quinone as photoproduct in dichloromethane and methanolic solution.

The kinetics of the rose Bengal (RB) sensitized photooxidation of 8-hydroxyquinoline in pH 6 aqueous solution and in organic media is reported by Pajares et al.[19], and have concluded that 8-OHQ is effectively photooxidised with O_2 (1Dg), faster if the OH group is ionised.

Bardez et al.[20,11] have reported excited-state processes in 8- hydroxyquinoline and photo-induced tautomerization and solvation effects observed in water.

The photo oxygenation of 8-HQ and some of their derivatives has been studied by Cossy and Belotti[18] 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 have been developed[22-25]. 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[26].

The present study reports the study of photosensitized reaction of 8-hydroxyquinoline and their derivatives with the cationic dye methylene blue (MB) as a photosensitizer, which has also been used as sensitizer in a number of photochemical reactions[27-30].

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.

The electron transfer reaction of methylene blue with imidazoline-2-ones in different solvents and at different pH and a complex formation of the sensitizer with the substrate in the excited state have been reported by Chawla et al.[31]

A number of studies have been reported on the photosensitization processes of methylene blue in the presence of the oxygen. Tanielian et al.[32] have reported the kinetic and mechanism study of the photosensitization by methylene blue in the presence of the oxygen. Silva et al.[33] 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[31-34].

Photooxidation of torpedo californica acetyl cholinesterase with methylene blue has been reported by Weiner et al.[35] Photooxidation of furanoeremophilane by methylene blue, rose bengal, toluidine blue and safranine T has been reported by Li et al.[36] Generation of singlet molecular oxygen by photosensitization with methylene blue (MB) supported in Nafion-Na films has been reported by Wetzler et al.[37] Photodynamic effect of MB under aerobic and anaerobic conditions has been reported by McCullagh and Robertson[38].

EXPERIMENTAL

The photosensitized reaction of the 8-Hydroxyquinoline in the presence of methylene blue in the alkaline medium have been studied in the visible light using a 100 W tungsten lamp for the irradiation. The photoproduct has been isolated and identified. The singlet state of the oxygen ($^{1}O_2$) participates in the photoreaction and photooxidation product is formed by oxidation of the substrates. 8-Hydroxyquinoline with methylene blue do 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 8-HQ 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.

RESULTS AND DISCUSSION

Spectral characteristics

The spectrums of the pure 8-hydroxyquinoline was recorded in the pH rang 2-12 in the range of 200-400 nm. The spectrum of the pure 8-hydroxyquinoline was recorded in the acidic medium. The pH of the solution 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 8-hydroxyquinoline show λ_{max} at 252 nm and 305-315 nm corresponding to π-π* and n-π* transition, respectively. The spectrums of the pure 8-HQ was recorded in the pH range 4-8 and λ_{max} of neutral form are observed at 239 nm and 285 nm for π-π* and n-π*, respectively. Spectrums of pure 8-hydroxyquinoline 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 8-hydroxyquinoline at 253 nm and 325-335 nm, respectively. Spectra of 8-HQ was recorded in the spectral range of 200-400 nm under experimental conditions against reagent blank.

The spectrum of the pure 8-HQ 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 8-hydroxyquinoline with different pH (Table 2) and measured λ_{max} and molar absorptivity are shown the spectrum of reaction mixture containing 8-HQ and methylene blue was recorded without exposing to the visible radiation and after exposure to the visible radiation in the pH range between 2 to12.

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. 8-HQ and methylene blue does not show reaction in the ground state. The spectrum of the reaction mixture of 8-HQ 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. 8-HQ show reaction on exposure to the visible radiation in the presence of MB. The 8-HQ exist in cationic (protonated) form at pH lower than 3 and it exist in the neutral form between pH 4 to 8 while 8-HQ exist in anionic (deprotonated) form between pH 9-12.

The photosensitized reaction of 8-HQ studied at pH 4 to 12 (Fig. 1). Absorption band at 253 nm (of 8-HQ) show decreases in the intensity and a new absorption band appears at 225 nm and 270 nm for 8-HQ as the photoreaction product formation takes place.

Table 1: Effect of pH on π-π* and n-π* transition and molar absorptivity some compounds

Compd.	Form	pH	π-π*	Experimental ε value	n-π *	Experimental ε value
8-HQ	Cation	2 pH	250 nm	31.300	305-315 nm	1435-1520
	Neutral	4-8 pH	239 nm	32.220	285 nm	2840
	Anion	9-12 pH	253 nm	30.010	325-335 nm	2816-2868

Table 2: Reported λ_{max} and molar absorptivity of 8-hydroxyquinoline at different pH

Compd.	Form	pH	π-π*	Reported ε value	n-π*	Reported ε value
8-HQ	Cation	2 pH	252 nm	31.600	305-320 nm	1480-1550
	Neutral	4-8 pH	240 nm	32.400	283 nm	2840
	Anion	9-12 pH	254 nm	30.130	325-340 nm	2820-2880

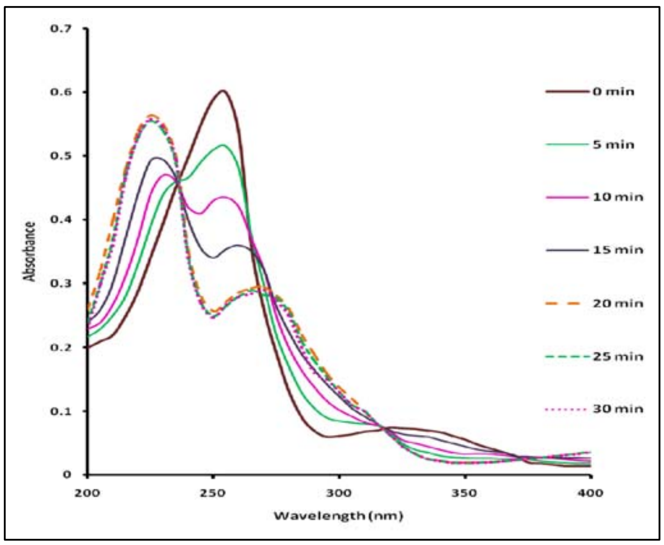


Fig. 1: Spectrum of 8-HQ and MB on exposure with time

Substrate: [8-HQ] = 2.0 x 10^{-5} M; Sensitizer: [MB] = 2.0 x 10^{-6} M; Light intensity = 11.18 E/S; pH = 11

Product study

The mass spectrum of the photoproduct of the 8-HQ in aqueous alkaline solution have been evaluated and compared with the reported mass spectrum and mass fragmentation of the Quinoline-5,8-quinone expected sample under experimental condition. The reaction product was isolated by extracting exposed solution 4 times with 5 mL 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 reaction product have been analyzed by mass spectrometric analysis by comparing mass spectrum with the reported data of Quinoline-5,8-quinone (Fig. 2).

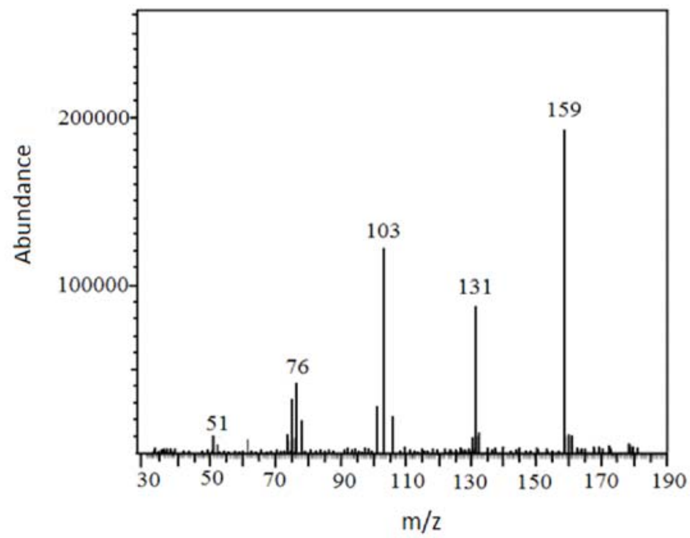


Fig. 2: Mass spectrum of the photoproduct of 8-HQ

The rate of the reaction

The reaction mixture containing substrate and sensitizer at pH 11 was exposed to the visible light. Absorption band for 8-HQ at 253 nm decreases and the absorbance bands at 220 nm and 270 nm increases corresponding to the photoproduct. The decrease of the absorbance at the λ_{max} 253 nm have been measured at different time intervals; which becomes constant after 30.0 min indicating the completion of the reaction. The results of a typical run for 8-Hydroxyquinoline have been presented. The decrease of the absorption for 8-HQ at 253nm and for have been used to calculate the rate constant for reaction. The rates of the photosensitized reaction for 8-hydroxyquinoline have been calculated (Table 3). A plot of 2 + log (O.D.) with time was prepared and slope was determined. The rate constant was calculated by following formula.

$$\text{Rate constant} = 2.\ 303 \times \text{Slope}$$

The photosensitized reaction rate for 8-HQ in experimental conditions show in (Table 3).

Table 3: Rate of the reaction of 8-hydroxy qunoline

Compound	Rate of the reaction (k) × 10^3 mol L^{-1} min^{-1}
8-HQ	46.8

The effect of variables on the rate of the reaction

The effect of the pH

The photosensitizer effect of methylene blue on 8-HQ have not been observed in the acidic medium upto pH 3 but the reaction is observed when pH becomes 4 and rate constant of the photosensitized reaction have been calculated for 8-HQ 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.

The effect of the concentration of the sensitizer

The effect of different concentrations of methylene blue on the rate of photosensitized reaction was studied. The rate constant was determined for 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 decreases at higher concentration of the sensitizer, which may be due to higher deactivation effect of the sensitizer at the higher concentration.

The effect of the concentration of the substrate

The effect of different initial concentrations of 8-HQ on the rate of the reaction was studied in the concentration range of 1 x 10^{-5} M – 3.5 x 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.

The effect of the light intensity

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.

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

Intensity of light I × 108 E/S	Rate of the reaction (k) × 10^3 mol L^-1 min^{-1}
	8-HQ
4. 85	17.5
6. 87	26.5
11. 18	46.8

The effect of the anaerobic condition

Study was carried out to observe the effect of oxygen concentration on the rate of the reaction. A purified nitrogen gas was passed through the solution of 8-HQ and MB for 20 min to remove dissolved oxygen of the solution. Maximum deoxygenated reaction mixture of the 8-Hydroxyquinoline and MB was exposed to the visible light.

The rate of the reaction was calculated. It decreases in the anaerobic condition. Quantum yield of the photosensitized reaction was calculated and it shows decrease in the anaerobic condition (Table 5).

Table 5: Effect of anaerobic condition on the rate of the reaction (Study of the role of singlet oxygen) and quantum efficiency of 8-hydroxy qunoline

Rate of the reaction (k) × 10^3 mol L^{-1} min^{-1}		Quantum efficiency (ϕ)	
Aerobic condition	Anaerobic condition	Aerobic condition	Anaerobic condition
46.8	1.08	0.314	0.0305

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 8-Hydroxyquinoline. 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 8-Hydroxyquinoline has been reported by Cossy and Belotti[18] 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 8- hydroxyquinoline was studied by changing the medium from aqueous alkaline to methanolic alkaline. 8-HQ show absorbance bands of π-π* and n-π* transition at 253 nm and 325-335 nm in the alkaline methanol.

The rate of the reaction slightly decreases in the case of 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 8-HQ does not proceed via a free radical intermediate formation in methanolic solution and rate of the reaction calculated (Table 6).

Table 6: Effect of solvent on the rate of the reaction of 8-hydroxy qunoline (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
8-HQ	46.8	41.5

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 substrate. It was also determined in the anaerobic condition (Table 7).

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.

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 and concentration of the oxygen plays an important role in the product formation.

Table 7: Quantum efficiencies of 8-hydroxy quinoline and derivatives

Compound	Φ value
8-HQ	0.314

The solution of the 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 8-HQ do not undergo photosensitized reaction. 8-HQ 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 8-HQ in the presence of sensitizer MB. The 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 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 and 8-HQ on exposure to the visible light. The anionic form of 8-HQ show absorption band at 253 nm and 255 nm, which decrease in intensity and a new absorption band appear at 225 nm and 270 nm on exposure to the visible light in the presence of MB.

The photosensitized reaction of 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[42-44]. There was no interaction between MB and 8-HQ without exposure to the visible radiation. The rates of the reaction calculate for 8-HQ methanolic alkaline solution, which are compare to aqueous alkaline solution of 8-HQ.

Reaction of the 8-HQ 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 8-HQ 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 8-HQ to give the photoproduct. Reaction of 8-Hydroxyquinoline with the singlet molecular oxygen ($^1O_2$) in the mixture containing methylene chloride and methanol has been reported by Amarasekara[17]. Mass spectroscopy data of the 8-HQ compared with the reported mass data of the Quinoline-5, 8-quinone the photoproduct, which suggest that Quinoline-5, 8-quinone for 8-HQ is the only photoproduct. The photoreaction product of the 8-HQ and their derivatives and MB were isolated, purified and analyzed. The m/z values of photoproduct are listed in Table 8.

Table 8

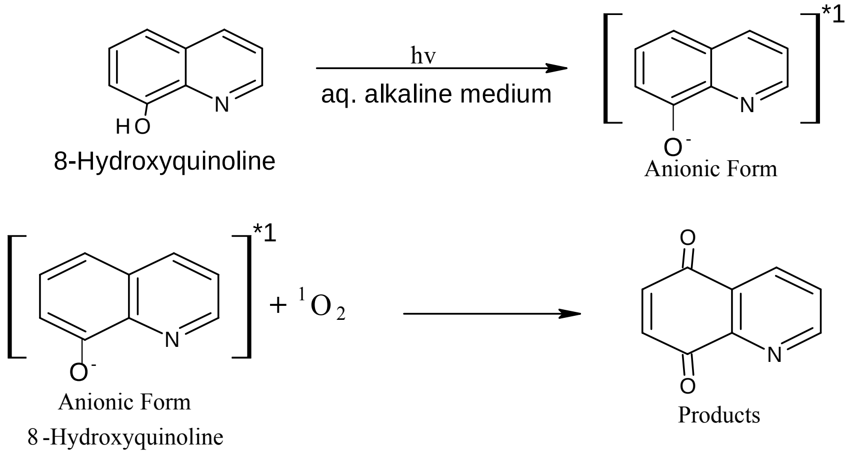
Compound	**The photoproduct of 8-hydroxyquinoline**				
Fragment ions	$C_9H_5NO_2$	$C_9H_9N^+$	$C_7H_5N^+$	$+ C_6H_4$	C_3HN^+
m/z Value	159.0	131.0	103.0	76.0	51.0

Mechanism: Photosensitized oxidation of 8-hydroxyquioline

$$MB \xrightarrow{h\nu} MB^{*1}$$

$$MB^{*1} \xrightarrow{ISC} MB^{*3}$$

$$MB^{*3} + {}^3O_2 \longrightarrow {}^1O_2$$



CONCLUSION

The anionic form of 8-Hydroxyquinoline do not show spectral changes on the exposure to the visible light of photosensitized reaction. The 8-Hydroxyquinoline existence is equilibriums in neutral and anionic form. The anionic form of 8-Hydroxyquinoline undergo photosensitized oxidation reaction in presence of methylene blue in the alkaline medium. Spectral profile of the exposed solution suggests that product of reaction is quinoline-5,8-quinone. The photoreaction is observed in methanolic solution of 8-Hydroxyquinoline suggesting do not free radical formation occurs. The photoreaction do not takes place in the anaerobic condition suggest 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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