



THE PHOTOCITIZED REACTION AND MECHANISM OF 8-HYDROXY QUINOLINE-5-SULPHONIC ACID USING METHYLENE BLUE (MB) AS PHOTOCITIZER

KRUPA PINAKINBHAI JANI*

Government Science Collage, GANDHINAGAR (Guj.) INDIA

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ABSTRACT

The photocitized reaction of 8-hydroxyquinoline 5-sulphonic acid has been studied in the alkaline medium in the visible light using Methylene blue (MB) as photocitizer. 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 photocitized 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 photocitized 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 photooxidation products are formed by oxidation of the substrates. The reaction has been studied using UV-visible spectroscopy and product analyzed with Mass-spectrometry.

Key words: Photocitized reaction, Methylene blue, 8-Hydroxyquinoline-5-sulphonic acid, Rate of reaction.

INTRODUCTION

The sulfate salt of 8-hydroxyquinoline (8-Hydroxyquinoline-5-sulphonic acid, 8-HQ-5-SA) is used as a complexing agent¹. 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-5-SA tautomerization were carried out by Li and Fang³. It is used in preparing antiseptics, deodorants, antiperspirants, preservatives⁴⁻¹³. The direct oxidation of 8-Hydroxyquinolinn and their derivatives have been reported by Bock et al.¹⁴ using sodium nitrite and gives quinoline-5,8-quinone in very low yield.

The kinetics of the thermal oxidation of 8-Hydroxyquinoline and their derivatives is reported by Palaniappan et al.¹⁵ and Amarasekara¹⁶ has reported the dye-sensitized photo oxidation reaction of 8-hydroxyquinoline or 5-hydroxyquinoline¹⁷ and Cossy & Belotti¹⁷ 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 and their derivatives in pH 6 aqueous solution and in organic media is reported by Pajares et al.¹⁸ and have concluded that 8-OHQ is effectively photooxidised with O₂ (1Dg), faster if the OH group is ionised.

Bardez et al.^{19,20} have reported excited-state processes in 8-hydroxyquinoline and their derivatives photo induced tautomerization and solvation effects observed in water. Jiang and Xue et al.²² have reported the preparation of Tris (8-hydroxyquinoline-5-sulfonic acid) Iron (III) complex and photocatalytic property of surface modified TiO₂. The Fe(HQS)₃ complex was characterized by elemental analysis, IR, nuclear magnetic resonance (NMR) and Raman spectrum. The Photo oxygenation of 8-HQ-5SA has been studied by Janine Cossy and Damien Belotti²³ and quinoline-5,8-quinone was obtained as oxidized photoproduct and the structure of the product was conformed using Mass-spectrometry, ¹H NMR and ¹³C NMR methods. A number of reagents or methods suitable for the preparation of substituted quinoline-5,8-quinones has been developed²³⁻²⁶. Among these, the most widely used oxidizing agent for the transformation of substituted 8-hydroxyquinolines to substituted quinoline-5,8-quinones is Fremy's salt²⁷.

The present study reports the study of photosensitized reaction of 8-hydroxyquinoline-5-sulphonic acid with the cationic dye methylene blue (MB) as a photosensitizer which has also been used as sensitizer in a number of photochemical reactions²⁹⁻³⁴. Several molecular complexes have been reported in the literature by electron transfer process between methylene blue and different compounds. Enescu et al.³⁵ have reported a pico-second transient absorption study for the excited state deactivation mechanism of methylene blue-nucleotide complexes and have also reported the classical molecular dynamics simulation method for the study of the electron transfer occurring in the optically excited state of methylene blue-guanine complex in water³⁶.

The electron transfer reaction of methylene blue with imidazole-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.³⁷ A number of studies have been reported on the photosensitization processes of methylene blue in the presence of the oxygen. Tanielian et al.³⁸ have reported the kinetic and mechanism study of the photosensitization by methylene blue in the presence of the oxygen. Silva et al.³⁹ 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 literature⁴⁰⁻⁴⁷. Photodynamic effect of MB under aerobic and anaerobic conditions has been reported by McCullagh C. et al.⁴⁸ Lin C et al.^{49,50} have reported methylene green photosensitized reduction (dechlorination) of DDT using visible light and methylene blue photosensitized dechlorination of perchloro ethylene.

EXPERIMENTAL

The photosensitized reaction of the 8-Hydroxyquinoline-5-sulphonic acid in the presence of methylene blue in the alkaline medium has 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 (¹O₂) participates in the photo reaction and photooxidation product is formed by oxidation of the substrates. 8-Hydroxyquinoline-5-sulphonic acid 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 8-HQ-5-SA 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 DICCUSSION

Spectral characteristics

The spectrum of the pure 8-Hydroxyquinoline-5-sulphonic acid was recorded in the pH rang 2-12 in the range of 200-400 nm. The spectrum of the pure 8-hydroxyquinoline-5-sulphonic acid was recorded in the acidic medium. The pH of the solution was maintained using suitable concentration of HCl. The -OH group gets protonated to $-\text{OH}_2^+$ up to pH 3 and shows λ_{max} of cationic form of 8-hydroxyquinoline-5-sulphonic acid show λ_{max} at 253 nm & 305 nm-315 nm corresponding to $\pi-\pi^*$ and $n-\pi^*$ transition, respectively. The spectrum of the pure 8-HQ-5-SA was recorded in the pH range 4-8 and λ_{max} of neutral form are observed at 240 nm & 305 nm for $\pi-\pi^*$ and $n-\pi^*$, respectively. Spectrum of pure 8-Hydroxyquinoline-5-sulphonic acid 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 $-\text{O}^-$ in the pH above 8. The absorbance bands corresponding to $\pi-\pi^*$ and $n-\pi^*$ transition for 8-Hydroxyquinoline-5-Sulphonic acid at 255 nm & 345 nm-335 nm, respectively. A spectrum of 8-HQ-5-SA was recorded in the spectral range of 200-400 nm under experimental conditions against reagent blank.

The spectrum of the pure 8-HQ-5-SA show 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-HQ-5-SA with different pH (Table 2) and measured λ_{max} & molar absorptivity are shown the spectrum of reaction mixture containing 8-HQ-5-SA and methylene blue was 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 hrs 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-5-SA and methylene blue does not show reaction in the ground state.

Table 1: Effect of pH on $\pi-\pi^*$ & $n-\pi^*$ transition & molar absorptivity 8 HQ-5-SA

Compound	Form	pH	$\pi - \pi^*$	Experimental ϵ value	$n-\pi^*$	Experimental ϵ value
8HQ-5-SA	Cation	2 pH	253 nm	34,050	305-315 nm	1600-1670
	Neutral	4-8 pH	240 nm	35,100	305 nm	2990
	Anion	9-12 pH	255 nm	33,300	345-355 nm	1730-1850

Table 2: Reported λ_{max} and molar absorptivity of 8-HQ-5-SA at different pH

Compound	Form	pH	$\pi-\pi^*$	Reported ϵ value	$n-\pi^*$	Reported ϵ value
8-HQ-5-SA	Neutral	4-8 pH	240 nm	34,890	305 nm	3010

The spectrum of the reaction mixture of 8-HQ-5-SA and MB were recorded after exposure to the visible radiation in the pH range 2-12 against a reagent blank (Fig. 1). The spectra shows change in the absorption pattern with time. 8-HQ-5-SA shows reaction on exposure to the visible radiation in the presence of MB. The 8-HQ-5-SA 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-5-SA exist in anionic (deprotonated) form between pH 9-12. The photosensitized reaction of 8-HQ-5-SA studied at pH 4 to 12. Absorption band at 255 nm 8-HQ-5-SA show

decrease in the intensity and a new absorption band appear at 225 nm and 270 nm for 8-HQ-5-SA as the photoreaction product formation takes place.

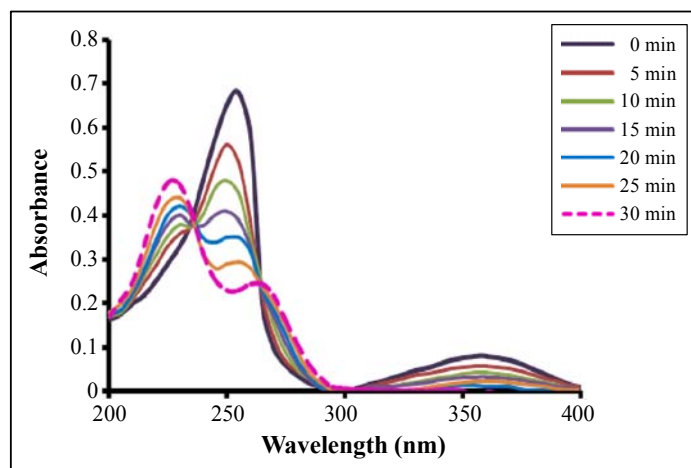


Fig. 1: Spectrum of 8-HQ-5-SA and MB on exposure with time

Substrate: $[8\text{-HQ-5-SA}] = 2.0 \times 10^{-5} \text{ M}$

Sensitizer: $[\text{MB}] = 2.0 \times 10^{-6} \text{ M}$

Light intensity = 11.18 E/S

pH = 11

Product study

The mass spectrum of the photoproduct of the 8-HQ-5-SA in aqueous alkaline solution has 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 has been analyzed by mass spectrometric analysis by comparing mass spectrum with the reported data of Quinoline-5, 8-quinone.

The rate of the reaction

The reaction mixture containing substrate and sensitizer at pH 11 was exposed to the visible light. The absorption band for 8-HQ-5-SA at 255 nm decreases and the absorbance bands at 220 nm and 270 nm of 8-HQ-5-SA increases corresponding to the photoproduct. The decrease of the absorbance at the λ_{max} 255 nm of 8-HQ-5-SA has been measured at different time intervals; which becomes constant after 30.0 min indicating the completion of the reaction.

The result of a typical run for 8-HQ-5-SA has been presented. The decrease of the absorption for 8-HQ-5-SA at 255 nm has been used to calculate the rate constant for reaction. The rate of the photosensitized reaction for 8-Hydroxyquinoline-5-Sulphonic acid has been calculated (Table 3). A plot of $2 + \log (\text{O.D.})$ 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 shows different rates for 8-HQ-5-SA in experimental conditions (Table 3).

Table 3: Rate of the reaction of 8-hydroxy quonoline-5-sulphonic acid

Compound	Rate of the reaction (k) $\times 10^3$ (mol L ⁻¹ min ⁻¹)
8HQ-5-SA	37.9

The effect of variables on the rate of the reaction

The effect of the pH

The photosensitizer effect of methylene blue on 8-HQ-5-SA has 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 has been calculated for 8-HQ-5-SA 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-5-SA taking MB in the concentration range of 1×10^{-6} M – 3.5×10^{-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-5-SA 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.

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-hydroxy quonoline-5-sulphonic acid

Intensity of light I $\times 10^8$ E/S	Rate of the reaction (k) $\times 10^3$ (mol L ⁻¹ min ⁻¹)
	8HQ-5-SA
4.85	12.0
6.87	20.0
11.18	37.9

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 8-HQ-5-SA and MB for 20 min to remove dissolved oxygen

of the solution. Maximum deoxygenated reaction mixture of the 8-HQ-5-SA 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 O₂, which suggests that oxygen participates in the photosensitized reaction of the 8-HQ-5-SA. Concentration of singlet oxygen (¹O₂) decreases in anaerobic condition. Therefore the oxidation decreases due to small concentration of the singlet state oxygen. Photochemistry of 8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline has been reported by Janine Cossy and Damien Belotti¹⁸ 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^{51,52}.

Table 6: Effect of anaerobic condition on the rate of the reaction of 8-hydroxy quinoline-5-sulphonic acid: Study of the role of singlet oxygen

Compound	Rate of the reaction (k) × 10 ³ (mol L ⁻¹ min ⁻¹)	
	Aerobic condition	Anaerobic condition
8HQ-5-SA	37.9	0.76

Table 7: Effect of anaerobic condition on the quantum efficiency of 8-hydroxy quinoline-5-sulphonic acid

Compound	Quantum efficiency (φ)	
	Aerobic condition	Anaerobic condition
8HQ-5-SA	0.236	0.0218

The effect of the solvent

The effect of the solvent on photosensitized reaction of the 8-HQ-5-SA was studied by changing the medium from aqueous alkaline to methanolic alkaline. The 8-HQ shows absorbance bands of π-π* and n-π* transition at 8-HQ-5-SA show absorbance bands at 255 nm & 345 nm-335 nm, respectively in the alkaline methanol. The reaction of 8-HQ-5-SA stops in the methanolic solution showing a strong free radical scavenging effects suggesting the formation of the free radical during the photoreaction. The photochemical product formation does not take place in 8-HQ-5-SA. The suppression of the reaction in presence of free radical scavenger suggests formation of free radical during the photoreaction of 8-HQ-5-SA. Methanol acts as free radical scavenger which inhibits the further reaction and photoproduct formation^{53,54} (Table 8).

Table 8: Effect of solvent on the rate of the reaction of 8-hydroxy quinoline-5-sulphonic acid: (Study of the free radical scavenging effect of methanol)

Compound	Rate of the reaction (k) × 10 ³ (mol L ⁻¹ min ⁻¹)	
	Aqueous alkaline solution	Methanolic alkaline solution
8HQ-5-SA	37.9	NIL

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 7). The plot of the ϕ value and the initial concentration of the substrate show a horizontal relationship with zero slope⁵⁵, 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 slope⁵⁵. 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 9: Quantum efficiencies of 8-hydroxy quinoline & derivatives

Compound	8HQ-5-SA
ϕ value	0.236

RESULTS AND DISCUSSION

The solution of the 8-HQ-5-SA 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 upto pH 3 remains the same as the control solution suggesting that the cationic form of 8-HQ-5-SA do not undergo photosensitized reaction. 8-HQ-5-SA with methylene blue at pH between 4 to 12 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-5-SA in the presence of sensitizer MB. The 8-HQ-5-SA 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-5-SA, which undergoes 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 molecule⁵⁵.

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-5-SA on exposure to the visible light. An anionic form of 8-HQ-5-SA show absorption band at 255 nm, which is decreases 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-5-SA completely stops in the methanolic medium, suggests the formation of a free radical⁵³⁻⁵⁴. The $-\text{SO}_3\text{H}$ react as free radical in 8-HQ-5-SA solution. There was no interaction between MB and 8-HQ-5-SA without exposure to the visible radiation. Reaction of the 8-HQ-5-SA 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 8-HQ-5-SA 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 ($^1\text{O}_2$). 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-5-SA to give the photoproduct. Reaction of 8-HQ-5-SA with the singlet molecular oxygen ($^1\text{O}_2$) in the mixture containing methylene chloride and methanol has been reported by A. S. Amarasekara¹⁷. Mass spectroscopy data of the 8-HQ-5-SA compared with the reported mass data of the Quinoline-5,8-quinone the photoproduct, which suggest that Quinoline-5, 8-quinone for 8-HQ-5-SA the only photoproduct. The photoreaction product of the 8-HQ-5-SA MB was isolated, purified and analyzed. The m/z values of photoproduct are listed in the given following Table.

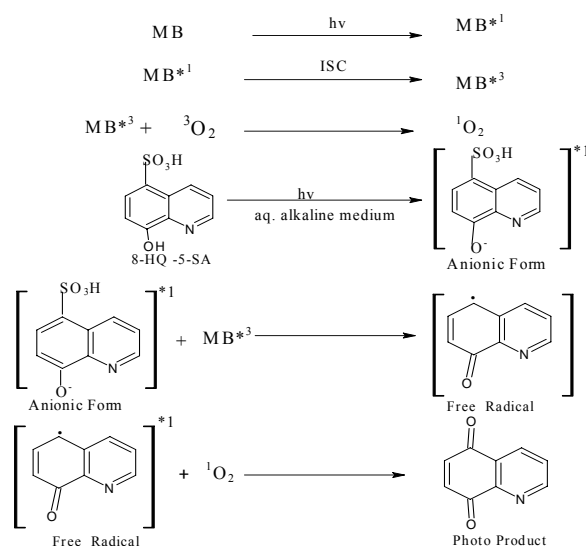
Table 10:

Compound	The photoproduct of 8-hydroxyquinoline & 8-hydroxyquinoline-5-sulphonic acid				
Fragment ions	C ₉ H ₅ NO ₂	C ₉ H ₉ N ⁺	C ₇ H ₅ N ⁺	C ₆ H ₄ ⁺	C ₃ HN ⁺
M/Z Value	159.0	131.0	103.0	76.0	51.0

Table 11:

Compound	The photoproduct of 2-methyl-8-hydroxyquinoline					
Fragment ions	C ₁₀ H ₈ NO ₂	C ₉ H ₄ NO ₂ ⁺	C ₉ H ₉ N ⁺	C ₇ H ₅ N ⁺	C ₆ H ₄ ⁺	C ₃ HN ⁺
M/Z Value	174.0	158.0	131.0	103.0	76.0	51.0

Mechanism



Photosensitized oxidation of 8-hydroxyquinoline-5-sulphonic acid

CONCLUSION

The anionic form of 8-HQ-5-SA do not show spectral changes on the exposure to the visible light of photosensitized reaction. The 8-HQ-5-SA existence is equilibriums in neutral and anionic form. The anionic form of 8-HQ-5-SA undergo 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 quinoline-5,8-quinone. The photoreaction is observed in methanolic solution of 8-HQ-5-SA 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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