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PHOTOSENSITIZED REACTION OF IMIDAZOLE

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ABSTRACT

The photosensitized reaction of imidazole has been studied in the alkaline medium in the visible light using methylene blue as a photosensitizer. 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 observed. The reaction has been studied in the anaerobic condition to observe the effect of the oxygen. Methanol shows free radical scavenging effect. The quantum efficiency of the photosensitized reaction has also been calculated. The scheme of the reaction mechanism has been suggested. The singlet oxygen ($^1O_2$) participates in the photoreaction and oxidized photo- product is formed. The reaction has been studied using UV-visible spectroscopy and product was analyzed Ion-Chromatography.

Key words: Photosensitized reaction, Methylene blue, Imidazole, Rate.

INTRODUCTION

Imidazole (glyoxaline) is an aromatic heterocyclic diazole and it is classified as an alkaloid having 5-membered planar ring, which is soluble in water and other polar solvents. It exists in two equivalent tautomeric forms, 1H-imidazole and 3H-imidazole, because the hydrogen atom can be located on either of the two nitrogen atoms. Many drugs contain an imidazole ring, such as antifungal drug nitroimidazole[1-3]. Imidazoles belong to the class of azole antifungal, which includes ketoconazole, miconazole, and clotrimazole. The imidazole nucleus forms the main structure of some well-known components of human organisms, i.e. the amino acid histidine, vitamin B12, a component of DNA base structure, purines, histamine and biotin. It is also present in structure of many natural or synthetic drug molecules.

Gadosy and McClelland have studied irradiation of 2-azido-1-methylimidazole in aqueous solution and obtained products from two reaction channels. One pathway involves a ring opening of azidoheterocycles and products are glyoxal bis-hydrate, the methyl ammonium ion, and cyanamide. The other pathway leads to the products that retain the five-member ring, the 2-amino-4,5-dihydro-4,5-dihydroxy-1-methylimidazolium ion[3] and its monophosphate ester.

Yuan[5] have reported synthesis of a series of symmetrical imidazole- and N-methylated imidazole-based diarylethenes, and their structures were characterized by NMR spectroscopy and mass spectrometry. The photochromism was investigated by UV/vis light irradiation in DMF solution[5]. Yuan et al.[6] reported the degradation of four pharmaceutical compounds (PhACs), ibuprofen (IBU), diphenhydramine (DP),

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phenazone (PZ), and phenytoin (PHT) by ultraviolet (UV) photolysis and UV/H_2O_2 process with a low-pressure UV lamp.

Su[7] has reported the theoretical reaction mechanism of photochemical transposition from pyrazole to imidazole. Caswell and Spiro[8] reported the ultraviolet Resonance raman Spectroscopy for aqueous solution of imidazole, imidazolium, 4-methylimidazole, histidine, histidinium, and Cu $(\text{imidazole})_4^{+2}$ with ultraviolet excitation by a H2-Raman-shifted Nd: YAG laser.

Kang and Foote[9] reported photosensitized oxidation of ^{13}C, ^{15}N-labeled imidazole derivatives and carried out a detailed mechanistic study of the photosensitized oxidation of isotope labeled imidazole derivatives. A new product and CO_2 was observed in the photooxidation of 2-H, N1-H imidazoles, but not in 2-substitituted imidazoles. Ryang and Foote et al.[10] have reported low-temperature NMR studies of photosensitized oxidation of imidazoles and observed 2, 5-endoperoxide as initial oxidation product. Wasserman et al.[11,12] have reported extensive studies on a variety of alkyl and aryl-substituted imidazoles.

Nohara et al.[13] reported that nitrogen-containing substrates such as amino acids, amides, succinimide, imidazole, hydroxylamine and urea were photodegraded in illuminated TiO_2 suspensions and the course of formation of NH_4^+ and NO_3^- ions has been monitored.

Peral and Gallego[14] reported the self-association of imidazole in aqueous solution, at different pH values by ultraviolet spectroscopy. The results obtained were discussed with respect to the structural domains of imidazole. The biological properties of imidazole require the knowledge of the self-association behavior of compound in aqueous solution and imidazole self-associate properties have been studied extensively in nonpolar solvents[15,16]. Sheu et al.[17] reported low-temperature photosensitized oxidation of a guanosine derivative and formation of an imidazole ring-opened product.

The study of photosensitized reaction of imidazole has been carried out with the cationic dye methylene blue (MB) as a photosensitizer. It has also been used as sensitizer in a number of photochemical reactions[18-23]. The process is based on the generation of singlet oxygen by photosensitization under alkaline pH.

$$\text{MB} + h\nu \rightarrow {}^1(\text{MB}) \qquad \ldots(1)$$

$${}^1(\text{MB}) + h\nu \rightarrow {}^3(\text{MB})^* \qquad \ldots(2)$$

$${}^3(\text{MB})^* + {}^3O_2 \rightarrow {}^1(\text{MB}) + {}^1O^*_2 \qquad \ldots(3)$$

The quenching of singlet oxygen by other species present in the solution, like hydroxy ions, generates hydroxyl radicals and superoxide anions as the predominant oxygen active species[24-26].

A number of studies have been reported on the photosensitization processes of methylene blue in the presence of the oxygen. Tanielian et al.[27] have reported the kinetic and mechanistic study of the photosensitization by methylene blue in the presence of the oxygen. Silva et al.[28] have reported photosensitization and oxidation of lysozyme in the presence of methylene blue.

Methylene blue photosensitized hydroxylation and oxidation with singlet oxygen has been reported in the literature[29-33]. Wetzler et al.[34] reported generation of singlet molecular oxygen by photosensitization with methylene blue (MB) supported in Nafion-Na films. Fontana et al.[35] reported methylene blue photosensitized oxidation of encephalin in the presence of nitrite. McCullagh Robertson[36] reported photodynamic effect of MB under aerobic and anaerobic conditions. Kuo and Ho[37] reported methylene blue combined Fenton-like process in the treatment of pesticides.

EXPERIMENTAL

The photosensitized reaction of the imidazole 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. Imidazole was photodegraded and a photoproduct was formed by oxidation in the presence of methylene blue in the alkaline medium. The singlet state of the oxygen ($^1O_2$) participates in the photoreaction of imidazole and photooxidation product is formed. Imidazole 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 Imidazole with time. The effects of the different parameters e.g. pH, concentration of the sensitizer, concentration of the substrate and the intensity of the light on the rate of the photosensitized reaction have been studied. 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 different excited states of the substrate molecule. The quantum efficiency has also been studied in the anaerobic condition.

The photoproduct has been analyzed with ion-chromatography. The retention time of the product has been compared with the standard sample. The mechanism of the photosensitized reaction has been suggested.

RESULTS AND DISCUSSION

Spectral characteristics

Spectrums of the pure imidazole was recorded in acidic, neutral and basic pH in the range of 200-400 nm. Spectra of the pure imidazole was recorded in the acidic medium. The pH of the solution was maintained using suitable concentration of HCl. The absorption band of imidazole at 210 nm corresponding to π-π^* transition in the pH 2-4. The spectrum of the pure imidazole was recorded in the pH range 4-8. Spectra of imidazole show λ_{max} at 210 nm and a lower molar absorptivity as compared to acidic pH.

The spectrum of the pure imidazole was recorded in the pH range 9-12. The pH of the solution was maintained using suitable concentration of NaOH. The absorbance band corresponding to π-π^* transition for imidazole was observed at 205 nm with higher molar absorptivity as compared to acidic pH. The spectra of imidazole was recorded in the spectral range of 200-400 nm under experimental conditions against reagent blank. Spectra of the some compounds show different form and molar absorptivity corresponding to different λ_{max} and reported values at acidic, neutral and basic pH (Table 1).

Spectrum of reaction mixture containing imidazole and methylene blue was recorded without exposing to the visible radiation and after exposure to visible radiation in the pH range (2-12). Spectrum of the reaction mixture was recorded after keeping the solution in the dark for 24 hours. The spectrum of the reaction mixture remains same as the solution of the substrate without exposure to the visible radiation. The reaction does not take place in the ground state of the methylene blue.

The spectrum of the reaction mixture of imidazole and MB was recorded after exposure to the visible radiation in the pH range 2-12 against a reagent blank. The spectrum does not show change in the absorption pattern in the pH range 2-6. Imidazole show reaction on exposure to the visible radiation in the presence of MB. The imidazole exists in protonated form at acidic pH and in neutral form between pH 4 to 8 while deprotonated form between pH 9-12 (Fig. 1). The reaction starts, when the pH of the solution becomes 8 and continues to increase as the pH of solution becomes more alkaline. It appears that only deprotonated species of imidazole undergoes photosensitized reaction. (Fig. 2). The absorption band of imidazole in the presence of methylene blue shows decreases in the intensity, when exposed to the visible light.

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

Compd.	Form	pH	π-π *	n-π*	Experimental ε value	Reported ε value
Imidazole	Cation	3 pH	210 nm	-	5,225	5,300
	Neutral	4-8 pH	210 nm	-	4,310	4,400
	Anion	9-12 pH	200 nm	-	9820	9,900

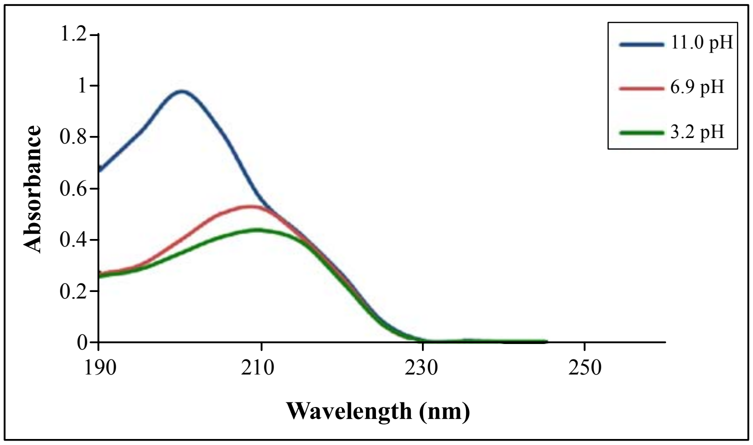


Fig. 1: Spectrum of imidazole at different pH in different forms [Imidazole] = 1.0 x 10^{-4} M

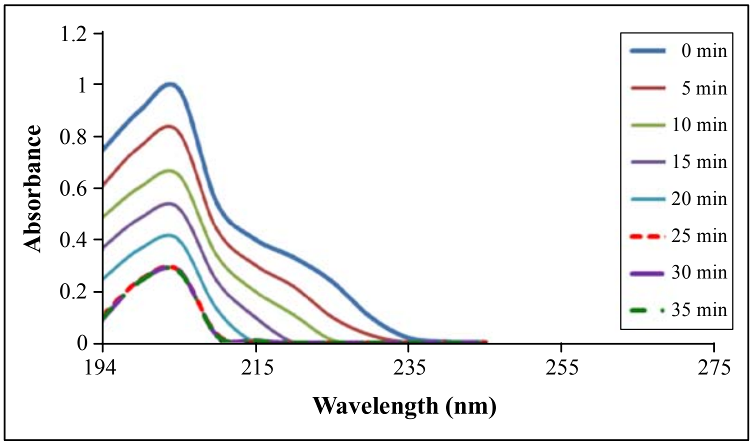


Fig. 2: Spectrum of imidazole and MB on exposure with time [Imidazole] = 1.0 x 10^{-4} M, [MB] = 1.0 x 10^{-5} M, Light intensity = 11.18 E/s, pH = 11)

Product study

The photodegraded product of imidazole in aqueous alkaline solution has been evaluated and analyzed by ion-chromatography. 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 10 µL of reaction solution of imidazole product was used for ion-chromatography analysis. The photoproduct of imidazole monitored by Dionex ICS-1000 instrument and suppressed conductivity ASRS-Ultra as detector with an Ion Pack- AS11-HC (4 × 250 mm) anionic column using a mobile phase as 30 mM NaOH.

The rate of the reaction

The reaction mixture containing substrate and sensitizer at pH 11 was exposed to the visible light. The absorption band of imidazole at 205 nm decreases in intensity and shows the formation of photo-degradation product. The decrease of absorbance at the λ_{max} 205 nm of imidazole has been measured at different time intervals, which becomes constant after some time indicating the completion of the reaction (Fig. 3). The results of a typical run for imidazole have been presented (Fig. 4).

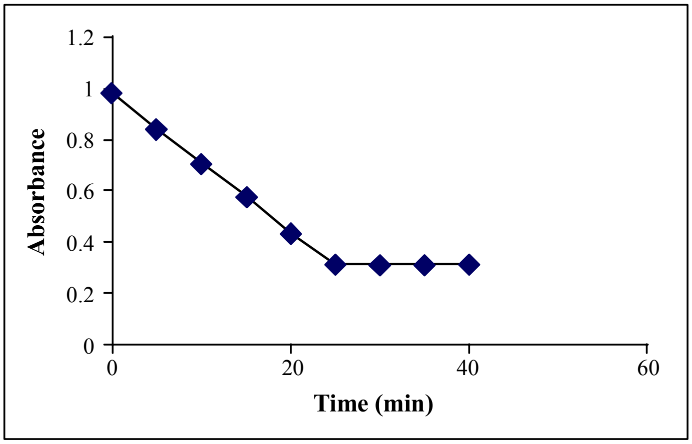


Fig. 3: Absorbance of imidazole and MB with exposure with time at λ_{max}

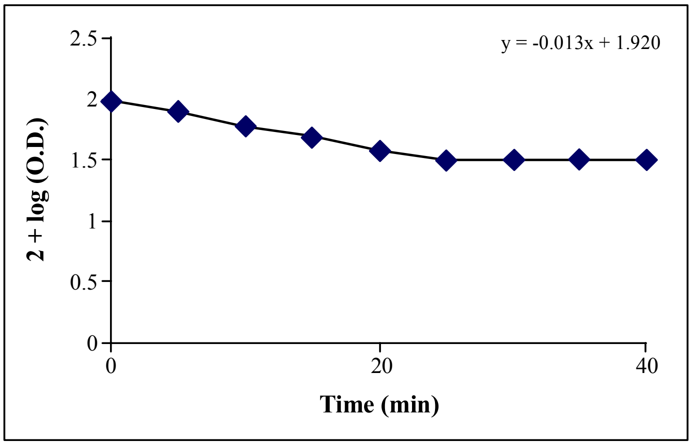


Fig. 4: Plot of log (O.D.) with time

The decrease of the absorption at 205 nm of imidazole has been used to calculate the rate constant for the reaction. The rate of the photosensitized reaction for imidazole have been calculated (Table 2). 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.

$$\text{Rate constant} = 2.303 \times \text{Slope}$$

Photosensitized reaction show different rates for different imidazole in experimental conditions (Table 2).

Table 2: Rate of the reaction of imidazole

Compound	Rate of the reaction (k) × 10^3 mol L^{-1} min^{-1}
Imidazole	45.13

Effect of the pH

The photosensitizer effect of methylene blue on imidazole has not been observed in acidic medium but the reaction was observed only in alkaline medium and rate constant of the photosensitized reaction has been calculated for imidazole in pH range 8-12. 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).

Effect of the concentration of sensitizer

The effect of different concentrations of methylene blue on the rate of photosensitized reaction was studied. The rate constant was determined for imidazole taking MB in the concentration range of 0.4×10^{-5} M -1.4×10^{-5} M. The rate of the reaction remains constant for this concentration range of 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 (Fig. 6).

Effect of the concentration of substrate

The effect of different initial concentrations of imidazole on the rate of reaction was studied in the concentration range of 0.4×10^{-4} M -1.4×10^{-4}M. The rate of the reaction remains constant in this concentration range of the substrate. The rate of the reaction is independent of the initial concentration of the substrate (Fig. 7).

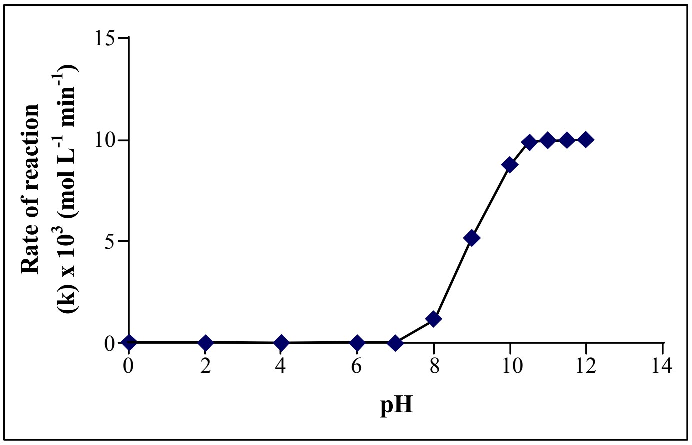


Fig. 5: Rate of the reaction of imidazole at different pH

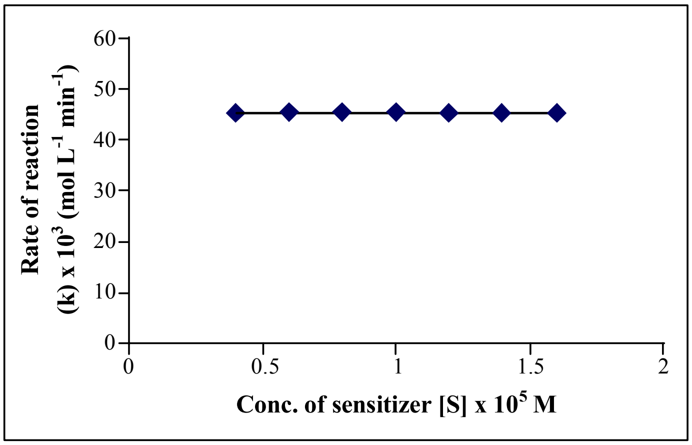


Fig. 6: Effect of the sensitizer concentration on the rate of the reaction

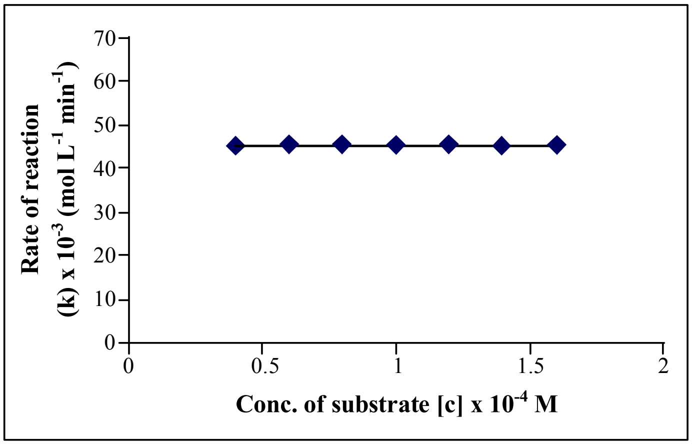


Fig. 7: Effect of the substrate concentration on the rate of the reaction

Effect of the light intensity

The increase of the light intensity [Einstein/second] (E/s) shows positive effect and rate of the photochemical reaction increases as the light intensity was increased. The number of excited molecules of the sensitizer increases with higher light intensity and correspondingly the rate of the reaction also increases. A linear relationship was observed between the light intensity and the rate of the reaction. The half-life of the reaction was calculated at different initial concentration of the substrate. $t_{1/2}$ Value was constant over the above range of the concentration and hence, the photochemical reaction is of the first order.

Effect of the anaerobic condition

Study was also carried out to see the effect of the oxygen concentration on the rate of the reaction. A purified nitrogen gas was passed through the solution of imidazole and MB for 20 min to remove dissolved oxygen of the solution. Maximum deoxygenated reaction mixture of the imidazole and MB was exposed to the visible light. The rate of the reaction was calculated. It decreases in an anaerobic condition (Table 3). Quantum yield of the photosensitized reaction was calculated and it shows a decrease in anaerobic condition (Table 4).

MB gets excited to the singlet state upon irradiation. The excited singlet state of MB undergoes inter system crossing (ISC) and forms triplet state, which transfers energy to the triplet state of oxygen to form singlet state oxygen. The singlet state oxygen is a good oxidizing agent. Photoreaction is dependent on the singlet state of the O_2, which suggests that oxygen participates in the photosensitized reaction of the imidazole. The hydroxyl radical ($^{\bullet}OH$) adduct of imidazole derivatives (Imi-OH) resulting from $^1O_2$-dependent generation of $^{\bullet}OH$ strengthened remarkably in the presence of methylene blue in alkaline medium[24-26]. This suggests that Imi-OH was produced in alkaline medium by methylene blue generation of $^{\bullet}OH$ from $^1O_2$. Concentration of the singlet oxygen ($^1O_2$) decreases in an anaerobic condition. Therefore, the oxidation decreases due to small concentration of the singlet state oxygen. Means and Feeney[38] have reported the effect of the singlet state oxygen imidazole generated by methylene blue. The formation of oxygen in different solvents and the different sensitizers has also been reported[39,40].

Table 3: Effect of anaerobic condition on the rate of the reaction of imidazole (Role of singlet oxygen)

Compound	Rate of the reaction (k) × 10^3 mol L^{-1} min^{-1}	
	Aerobic condition	Anaerobic condition
Imidazole	45.13	0.461

Table 4: Effect of anaerobic condition on the quantum efficiency of imidazole

Compound	Quantum efficiency (Φ)	
	Aerobic condition	Anaerobic condition
Imidazole	0.362	0.0362

The effect of the solvent (A free radical scavenger)

The effect of the solvent on photosensitized reaction of the imidazole was studied by changing the medium from aqueous alkaline to methanolic alkaline. Imidazole show absorbance bands at 205 nm in the alkaline methanol. The reaction mixture of imidazole does not show change in the absorbance on exposure with MB in the visible light in the alkaline methanolic solution. Methanol acts as a free radical scavenger and the photochemical product formation does not take place in imidazole[41-43]. The suppression of the reaction in the presence of a free radical scavenger suggests formation of free radical during the photoreaction of imidazole (Table 5).

Table 5: Effect of solvent on the rate of the reaction of imidazole (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
Imidazole	45.13	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 substrate (Table 6). It was also determined in the anaerobic condition. (Table 4).

The plot of the ϕ value and the initial concentration of the substrate (Fig. 8) shows a horizontal relationship with zero slope[44], which suggests 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 substrate molecule. The plot of the inverse of the quantum efficiency versus inverse of the concentration of the substrate is horizontal with zero slope[44], suggesting that the exciplex formation does takes place in the singlet excited state (Fig. 9). The quantum efficiency of an anaerobic reaction is less than quantum efficiency of aerobic reaction. It shows that the photosensitized reaction is less efficient in anaerobic condition. Concentration of the oxygen plays an important role in the product formation.

Table 6: Quantum efficiencies of imidazole

Compound	**Imidazole**
Φ value	0.362

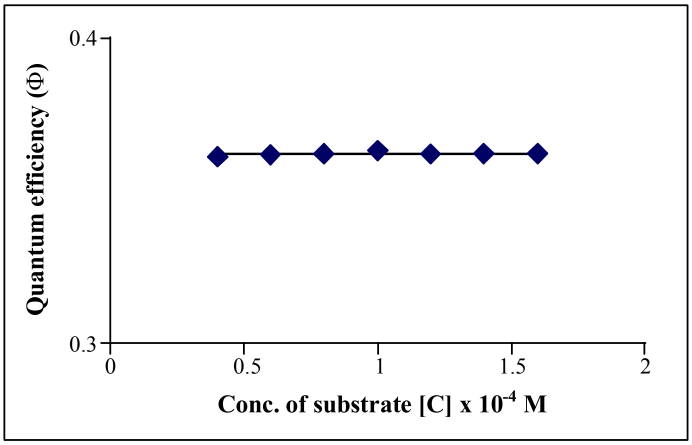


Fig. 8 Effect of the substrate concentration on the quantum efficiency

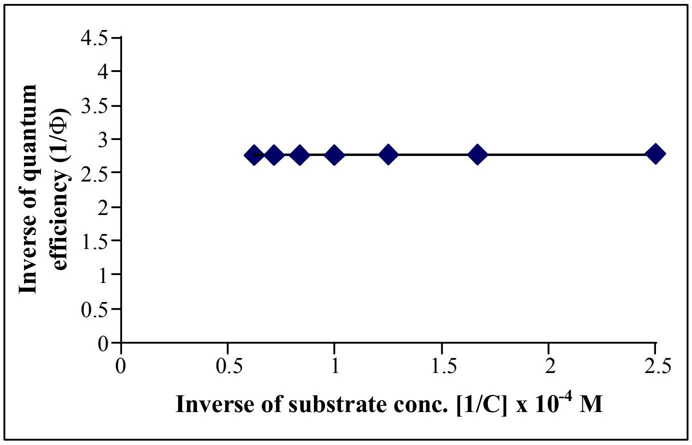


Fig. 9: Plot of inverse of the substrate concentration (1/[c]) versus inverse of the quantum efficiency (1/[Φ])

The spectrum of the exposed reaction mixture in acidic pH remains the same as the control solution. It suggests that the protonated form of imidazole does not undergo photosensitized reaction. Imidazole with methylene blue in alkaline pH between 8-12 shows spectral changes with time, when exposed to the visible light. This suggests that a photochemical reaction occurs in the deprotonated form of the imidazole in the presence of sensitizer MB. At basic pH, a stronger band appears at lower wavelength and an inflection near 211.0 nm. The n-π* band in imidazole was observed more readily in non-polar solvents than in polar solvents[45]. Cationic dye MB absorbs visible radiation and is excited to the singlet excited state, which transfers its energy to imidazole, which undergoes photochemical reaction.

Plot of the quantum efficiency versus concentration (Φ v/s C) shows a horizontal relationship with zero slopes, which suggests singlet state energy transfer from singlet excited state sensitizer molecule to the substrate molecule[44]. Plot of the inverse of the quantum efficiency versus inverse of the concentration of the substrate (1/Φ v/s 1/C) was also a straight line with zero slope. It suggests that no exciplex formation takes place between the excited state of cationic dye MB and imidazole on exposure to the visible light.

The deprotonated form of imidazole shows absorption band at 205 nm in the pH range 8-12. Imidazole was photo degraded and nitrate ion was observed, which was formed by oxidation in the presence of methylene blue in the alkaline medium. The decoloration of the methylene blue dye solution is due to the reaction of hydroxyl radicals, which can be generated due to dissociation of water molecule, or OH^- ion from the base[46-48]. Photosensitized reaction was carried out in the methanolic alkaline solution, which acts as free radical scavenger. The reaction stops in the alkaline methanolic solution[41,42]. The photoreaction involving a free radical formation does not occur in the presence of the methanol, a free radical scavenger. It appears that photoproduct formation takes place by imidazole and excited MB molecule involving a free radical[41-43]. A decrease in the rate of the reaction and also the quantum efficiency of the reaction in anaerobic condition suggests that product formation involves oxidation by singlet state of oxygen ($^1O_2$).

Methylene blue is excited to singlet excited state on exposure to the visible radiation. The singlet excited state of MB undergoes ISC and forms triplet state, which transfers the energy to triplet state of the oxygen to form singlet state oxygen. Singlet state oxygen produces hydroxyl radical by reaction with water molecule in the alkaline solution. The hydroxyl radical attacks 2-carbon atom of the imidazole ring, which gives the photoproduct of imidazole.

The ion chromatography data of photoproduct suggests the formation of NO_3^- ion as photoproduct in the reaction of imidazole. The photoreaction product of imidazole and MB were isolated, purified and analyzed. The photoproduct of imidazole was analyzed by ion-chromatography shows retention time of the product as nitrate ion (10.04 min), which are comparable with the standard sample of nitrate ion.

Peak name	**Time ECD.1 RT(min)**	
	Sample	**Standard**
Nitrate ion	4.739	4.740

Mechanism

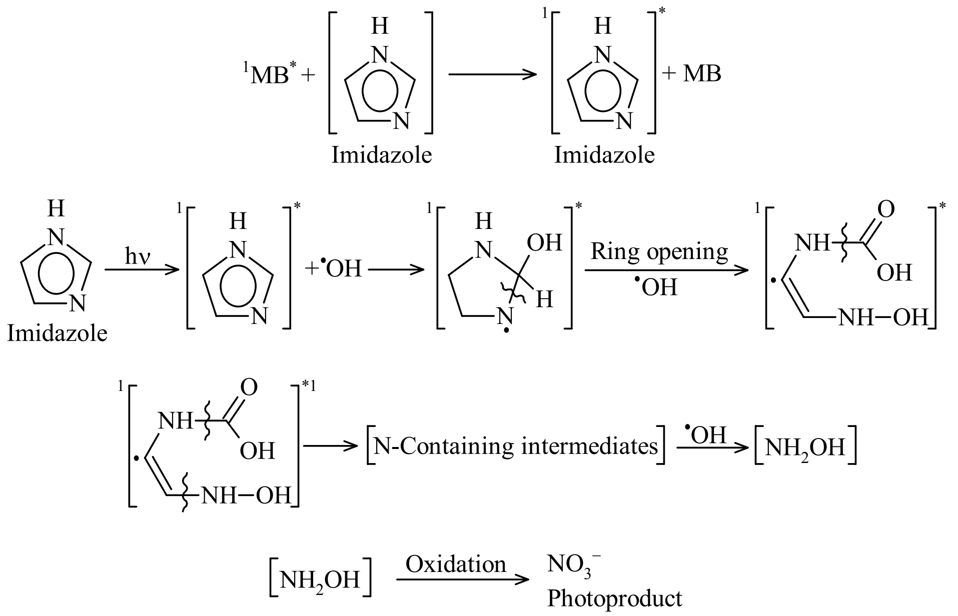
$$^1MB \longrightarrow MB^* \qquad ...(5)$$

$$^1MB^{*1} \xrightarrow{ISC} {}^3MB^* \qquad ...(6)$$

$$^3MB^* + {}^3O_2 \longrightarrow {}^1O_2 + MB \qquad ...(7)$$

$$^1O_2 + H_2O \longrightarrow {}^{\bullet}OH + {}^3O_2 \qquad ...(8)$$

Photosensitized oxidation of imidazole



CONCLUSION

The deprotonated form of imidazole does not show spectral changes on the exposure to the visible light in photosensitized reaction. The imidazole exists in equilibrium at neutral to basic pH. The form of imidazole undergoes photosensitized oxidation reaction in presence of methylene blue in the alkaline medium. The product formation takes place via an intermediate-hydroxyl free radical formation. The $^{\bullet}$OH radical formation takes place in alkaline medium by methylene blue from singlet oxygen.

The spectral profile of the exposed solution of imidazole suggests that photoproduct of reaction is nitrate ion. Photoreaction was not observed in methanolic solution of imidazole suggesting free radical formation. The photoreaction does not take place in the anaerobic condition suggesting that the singlet oxygen participates in the reaction. The rate of the reaction was dependent on pH and light intensity but it is independent of initial concentration of the substrate, sensitizer concentration and concentration of oxygen.

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