

RESEARCH ARTICLE

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Benzophenone: Mechanism and
Kinetics**

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Triplet-Triplet Energy Transfer Reaction of 5-Methylthiazole and Benzophenone: Mechanism and Kinetics

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Abstract

The photosensitized reaction of 5-Methylthiazole (5MT) with benzophenone (BP) in aqueous alkaline medium using visible light has been studied to mineralize 5MT to less toxic ions. 5MT shows the λ_{\max} at 240 nm in the pH range of 2-12. The triplet-triplet energy transfer from the triplet excited state of the aromatic ketone BP to the substrate molecule takes place during the photosensitized reaction. The triplet excited 5MT breaks down on further exposure and photoproduct formation takes place. The reaction shows the participation of singlet oxygen during the photoreaction. The sulfate has been observed as photoproduct. The apparent rate of the reaction has been calculated and the effect of pH, concentration of the sensitizer, the light intensity on the apparent rate of the reaction has been studied. The quantum efficiency of the photochemical reaction is calculated using potassium ferri oxalate actinometer and the effect of the concentration of the substrate on the quantum efficiency is calculated. The reaction mechanism and the excited states involved have been suggested.

Keywords: 5-Methylthiazole; photosensitized reaction; exciplex formation; singlet oxygen; dipole-dipole energy transfer mechanism.

1. Introduction

Nowadays many toxic organic compounds from different sources are discharged into the water bodies and the problems of water quality have become more important than the quantity of water. Toxicity of these compounds in a given environmental system depends on the transport and the degradation processes. To predict their fate in the natural environment and to assess their risk, it is necessary to improve our knowledge on their chemical reactions under environmental conditions. The classical biological oxidation methods failed to eliminate such micro pollutants to the desired level whereas physiochemical technique just transferred them from one phase to another without destroying them. Such classical biological oxidation methods and physiochemical techniques are useful only for the high level concentration of pollutants, but when the pollutants are present in traces such methods have failed to remove these pollutants from water bodies. Photochemical transformation is one of the major abiotic degradation pathways occurring in natural waters to convert this toxic compound into non-toxic material [1, 2] at a very trace level and has received increasing interest in the last three decades. Phototransformation of pollutants may take place through different pathways. Direct photolysis can occur if the considered pollutant absorbs solar radiation. However, the ability to undergo chemical changes after the absorption of photons is an intrinsic property of the molecule and can vary drastically from one compound to the other. Photoinduced transformations mediated by components of the aquatic environment can also occur. In particular, dissolved natural organic matter (DOM), absorbing a large portion of photons, is a potential photosensitizer. Singlet oxygen, superoxide ion/hydroperoxyl radicals, hydroxyl radicals and organic peroxy radicals were proved or proposed to be generated in natural waters under the influence of sunlight.

The structure of 5MT is composed of an exocyclic methyl group and a heterocyclic molecule that contains sulphur, nitrogen and carbon atoms. 5MT has been used as a pharmaceutical intermediate, pesticide intermediate and as a flavour ingredient in the food flavours, nut flavours, vegetable and vegetative flavours, baked goods, dairy products, beverages and hence, it has been frequently detected in both waste water treatment plant and surface water and can come into contact with potable water and can easily enters to food cycle. 5MT is harmful according to its Material Safe Data Sheet and exhibits persistence to microbial degradation. Therefore, 5MT is an aqueous pollutant of concern in water and wastewater systems.

Maurizio D' Auris [3] has reported the *ab initio* study on the isomerization of 2- phenylthiazole and 2-acetylthiazole. The photochemical isomerization of thiazole derivative involves the formation of the Dewar isomer. The irradiation of thiazole do not give product [4] but 2- methyl, 4-methyl and 5-methyl thiazole gave the corresponding isothiazole in trifluoroacetic acid. Pavlik *et al.* [5] have reported that the methylisothiazoles undergo phototransposition in neutral solution to methylthiazoles by a single permutation process. The isothiazole to thiazole transposition was observed to occur upon photolysis in a variety of solvent but the reverse transposition of thiazole to isothiazole is not observed. The energy of incoming solar spectrum, ultraviolet radiation ($\lambda < 400$ nm) accounts to only less that 4%, while the visible light is more than 50%. Hence, effective utilization of the visible light is an attractive area of photochemical research. The bond dissociation energy per mole for most of the molecules lies between 150 kJ and 600 kJ. These energies are available from Avogadro's number of photons of wavelengths lying between 800 nm and 200 nm respectively, which correspond to the visible and near ultraviolet regions of the electromagnetic spectrum. The same range of energies is required for electronic transitions in most atoms and molecules. Phototransformation of pollutants under natural conditions may be a complex process. In order to understand the mechanisms involved it is necessary to investigate photosensitized transformations under relevant experimental conditions.

In the present work, we focused on the photosensitized reaction of the 5MT in the aqueous alkaline medium on irradiation with visible light. The aromatic ketone, benzophenone has been used as photosensitizer. The kinetics of the photodegradation reaction has been studied. The effects of the pH, the concentration of the sensitizer, the concentration of the substrate and the light intensity have been evaluated on the rate of the reaction. The reaction has been used to determine the quantum efficiency and whether the reaction is monophotonic or biphotonic. The scavenging technique was used to evaluate the role played by free radical and singlet oxygen and to assess the mechanisms involved in the light-induced reactions.

2. Methods

5MT, BP, potassium trioxalate ferrate, ammonium ferric sulphate, sodium acetate, phenanthroline, were used as received. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were of analytical grade. Ethyl alcohol was HPLC grade. All chemicals were used as received. Water was doubly distilled. The solutions were kept in dark at room temperature and were diluted as per the requirement.

100 W tungsten filament light source has been used for the exposure of the sample solution, convex lens is used to converge the irradiation and a glass water jacket is used to decrease the temperature of the solution. Light intensity is measured using "Light intensity measurement meter" (Iwiss Solar, Model Number: TM206). All the spectral measurements have been carried out on UV-Vis spectrophotometer (Chemito – 2100). The pH was adjusted by addition of HCl or NaOH solutions, respectively and has been measured using pH-meter (Systronics, India) with glass calomel electrode.

The four sets of 5MT solution (2.0×10^{-4} mol L⁻¹) in alkaline aqueous medium were prepared. Two of them contain BP (1×10^{-4} mol L⁻¹) as a photosensitizer. Two flasks, one containing BP and the other without BP were kept in dark for 24 hours while remaining similar flasks were exposed to the visible light from 100 W tungsten lamp. The course of the reaction was followed by recording the spectrum of the exposed solution with a control solution in the range of 200-300 nm against reagent blank. The flask kept in the dark and the flask exposed without sensitizer did not show difference in the spectrum when compared to the control; while the exposed flask containing sensitizer showed depletion in λ_{\max} .

The effect of varying concentration of BP (in the range of 0.6×10^{-4} mol L⁻¹ to 1.6×10^{-4} mol L⁻¹) and 5MT (in the range of 1.6×10^{-4} mol L⁻¹ to 2.4×10^{-4} mol L⁻¹) on the apparent rate of the reaction has been studied respectively. The solutions were deaerated or saturated with O₂ by purging with nitrogen or O₂ respectively, for 30 min via a needle through the cap. The effect of the free radical scavenger on the photo sensitized reaction was studied by changing the medium from aqueous alkaline to methanolic alkaline. Light intensity can be varied by changing the distance of the sample solution from the tungsten lamp source, and intensity was measured using "Light intensity measurement meter". The study was carried out at room temperature and pressure. The quantum yield of the photo reaction has been evaluated using potassium ferrioxalate actinometer.

3. Results and Discussion

3.1 Spectral characteristics

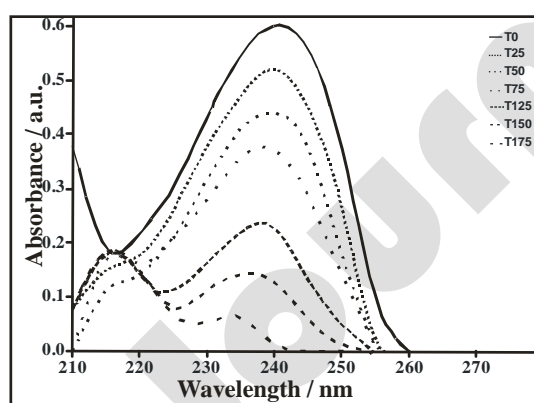
Experiment shows that the 5MT (2×10^{-4} mol L⁻¹) exhibits one well-defined maxima for $\pi \rightarrow \pi^*$ transition at 240 nm (molar absorptivity = $3,000$ L mol⁻¹ cm⁻¹) between the pH range 2–12. Substitution of proton by a

methyl group in the azole ring alters the absorption spectrum of thiazole. It induces bathochromic with significant increase in the absorption intensity.

5MT has been reported not to undergo transposition upon irradiation in a variety of neutral solvents. Pavlik *et al.* [5] have reported the formation of 2-Methylisothiazole from the irradiation of 5MT in TFA solvent at 254 nm under nitrogen at ambient temperature, however, in the present study, 5MT was found to be photo stable in acidic as well as in the alkaline medium, when irradiated by visible light. It was also found during the experiment that 5MT and BP don't interact in the ground state but when the reaction mixture containing 5MT ($2 \times 10^{-4} \text{ mol L}^{-1}$) and BP ($1 \times 10^{-4} \text{ mol L}^{-1}$) maintained at different pH between 2 to 12 were exposed to the visible radiation and the spectra were recorded against the reagent blank, the reaction mixture does not show any significant change in the pH range 2–6 but it undergoes photoreaction in the pH range of 8–12.

The changes of the absorption spectrum were plotted against time which show decrease at the λ_{max} 240 nm (**Figure 1**) and remains constant after 175 min exposure indicating the completion of the reaction. Isosbestic point was not observed and this indicates that the reaction does not consist just in the transformation of one species to another.

Figure 1: Absorption spectra ((A) at T_0 , (B) at T_{25} , (C) at T_{50} , (D) at T_{75} , (E) at T_{125} , (F) at T_{150} , (G) at T_{175}) of the photosensitized reaction of 5MT with BP, 5MT: $2 \times 10^{-4} \text{ mol L}^{-1}$, BP: $1 \times 10^{-4} \text{ mol L}^{-1}$, time interval: 25 mins, 100 W tungsten lamp, pH 11.



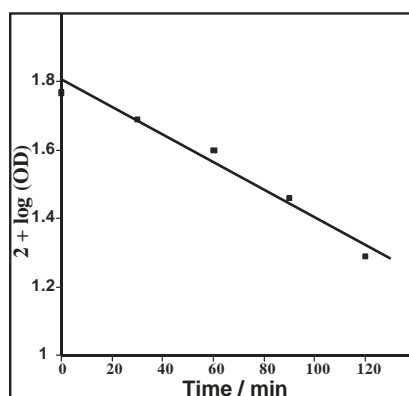
3.2 Determination of the apparent rate constant and effect of different parameters on apparent rate constant

The reaction follows the first order reaction kinetics as the plot of $2 + \log \text{OD}$ (optical density) vs. time (at 240 nm) is a straight line with a positive slope (**Figure 2**). The rate constant (apparent k value) has been determined by the expression:

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

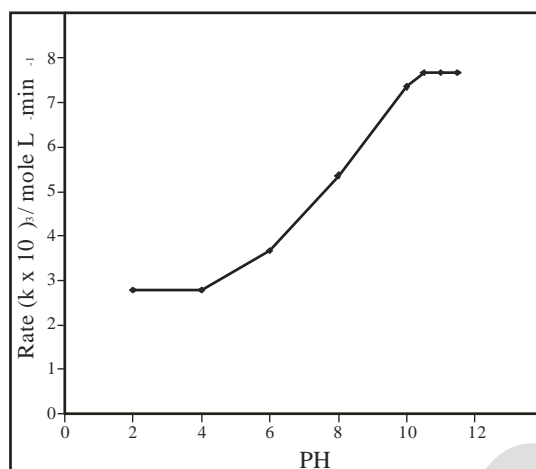
The half life of the reaction has been observed at different concentrations of the substrate and $t_{1/2}$ value is constant over the above range of the substrate concentration.

Figure 2: $[2 + \log \text{OD}]$ vs. time plot of the photosensitized reaction of 5MT with BP on exposure at 240 nm, 5MT: $2 \times 10^{-4} \text{ mol L}^{-1}$, BP: $1 \times 10^{-4} \text{ mol L}^{-1}$, time interval: 25 mins, 100 W tungsten lamp, pH 11.



3.2.1 Effect of the pH

Figure 3: Effect of the pH on the apparent rate of the reaction measured at 240 nm, 5MT: $2 \times 10^{-4} \text{ mol L}^{-1}$, BP: $1 \times 10^{-4} \text{ mol L}^{-1}$, time interval: 25 mins, 100 W tungsten lamp, pH 11.



The spectrum of 5MT was recorded at several pH values ranging from 2 to 12, while keeping the concentration of 5MT as constant. The absorbance at λ_{max} 240 nm was plotted against the pH of the solution. The centre of the sigmoidal curve gave the pKa value of 3.27 ± 0.05 for 5MT which is sufficiently basic to be protonated in TFA.

In this investigation, the effect of the pH value on the 5MT photo degradation with BP in aqueous medium was studied in the pH interval range from 2 to 12. Figure 3 showed the dependence of apparent k value for 5MT degradation on the pH in the presence of $1 \times 10^{-5} \text{ mol L}^{-1}$ BP, under $15 \times 10^8 \text{ E/s}$ visible light intensity. The photo effect of benzophenone is sensitive to OH^- ion concentration of the solution; therefore the increase in OH^- ion concentration increases the sensitivity of the sensitizer, which shows higher proton abstraction capability of benzophenone. Similar effect of OH^- ion concentration has been observed in the present study.

3.2.2 Effect of the initial concentration of sensitizer

Figure 4: Effect of the sensitizer concentration on the apparent rate of the reaction at 240 nm, 5MT: $2 \times 10^{-4} \text{ mol L}^{-1}$, BP: $0.6 \times 10^{-4} \text{ mol L}^{-1}$ to $1.6 \times 10^{-4} \text{ mol L}^{-1}$, time interval: 25 mins, 100 W tungsten lamp, pH 11.

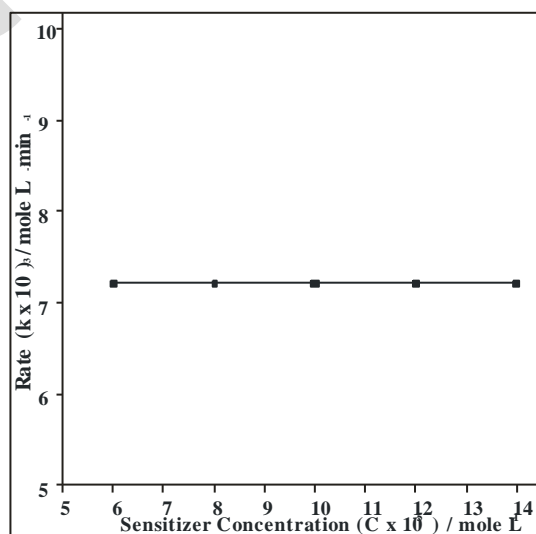


Figure 4 showed the dependence of apparent k value of the photodegradation of 5MT on the initial concentration of sensitizer under 15×10^8 E/s visible light irradiation. The results showed that the photo degradation of 5MT did not occur in the absence of BP. However, 5MT degradation could be efficiently enhanced in the presence of BP. 5MT has its λ_{\max} below 400 nm and is not photodegraded directly by the visible light. Triplet energy of benzophenone is 69 kcal/mole, which on collision with the 5MT transfers energy to it. The first-order apparent kinetic constant (k) for 5MT degradation increased with increasing sensitizer concentration and then becomes constant with increasing sensitizer concentration. However, the first-order kinetic constant for 5MT degradation decreased as the BP concentration reached above a threshold level where the self deactivation of the sensitizer molecule takes place by intermolecular collision. Therefore, the optimal sensitizer concentration value was 1.0×10^{-4} mol L⁻¹ which mostly favoured the photo degradation of 5MT in the experimental condition.

3.2.3 Effect of the initial concentration of substrate

The first-order apparent kinetic constant k remains the same 7.79×10^{-3} min⁻¹ with increasing substrate concentration from 1.6×10^{-4} mol L⁻¹ to 2.4×10^{-4} mol L⁻¹ and decreases slightly for higher concentration of substrate. Obviously, there should be an optimal concentration of substrate (2×10^{-4} mol L⁻¹) for 5MT degradation. The first-order apparent kinetic constant k remaining constant in this concentration range shows that this reaction is independent of the initial concentration of the substrate.

3.2.4 Study in aerobic and anaerobic conditions to check a possible involvement of singlet oxygen

The reaction was studied in the anaerobic condition to observe the participation of singlet oxygen during the photosensitized reaction. The benzophenone (photo sensitizer) absorbs the visible radiation and goes to the singlet excited state and is converted to the triplet state by intersystem crossing (ISC). The excitation energy of the sensitizer molecule is transferred to ³O₂ molecule and converts it to the singlet state, while photo sensitizer molecule returns to the ground state. This singlet oxygen is a highly reactive species which gives the photo oxygenation reaction. Benzophenone is reportedly efficient sensitizer for the conversion of triplet oxygen to singlet oxygen in the presence of light [6-9]. The first-order apparent kinetic constant was calculated for the exposed solutions of the different concentration of the substrate [5MT] and the sensitizer BP in the aerobic as well as in the anaerobic condition. The first-order apparent kinetic constant in the aerobic condition 7.86×10^{-3} min⁻¹ at 240 nm decreases to 2.303×10^{-3} min⁻¹ at 240 nm in the anaerobic condition. The ϕ value of the reaction was also calculated in the anaerobic condition which shows decrease. These observations suggest that the participation of the singlet oxygen during the photo reaction is an important step and oxidation reaction takes place during the photo sensitized reaction.

3.2.5 Effect of the free radical scavenger

The effect of the free radical scavenger on the photosensitized reaction of 5MT was studied by changing the medium from aqueous alkaline to methanolic alkaline. The solutions of the different concentration of substrate [5MT] and the sensitizer BP were prepared in the alkaline methanolic solution and irradiated with the visible light. 5MT shows λ_{\max} at 240 nm in the alkaline methanolic solution. The first-order apparent kinetic constant for the 5MT degradation reaction in the aqueous alkaline medium was 7.67×10^{-3} min⁻¹ at 240 nm which changed drastically to 2.21×10^{-3} min⁻¹ at 240 nm in the alkaline methanolic solvent. The photochemical reaction shows sharp decrease in the alkaline methanolic solvent suggesting that there is free radical formation during the reaction.

3.2.6 Effect of the light intensity

Light intensity is another important factor to be considered during photochemical process. Generally, higher light intensity can lead to higher degradation rate for organic pollutants in photochemical reaction. The same results were obtained in this investigation as shown in Table 1. The solutions of the different concentration of the substrate [5MT] and the sensitizer BP were prepared in the aqueous alkaline solution and irradiated with the visible light of the different intensity. The increase of the light intensity [Einstein / second (E/s)] shows positive effect and the first-order apparent rate constant of the reaction increases as the light intensity increases. The increase in the number of photons increases the number of excited sensitizer molecule and the apparent rate of reaction also increases. A linear relationship has been observed between the light intensity and the first-order apparent rate constant of the reaction.

Table 1: Effect of the Light Intensity on the apparent rate of the reaction and on the quantum efficiency at 240 nm, 5MT: 2×10^{-4} mol L⁻¹, BP: 1×10^{-4} mol L⁻¹, time interval: 25 mins, 100 W tungsten lamp, pH 11.

Light Intensity (1×10^8) E/s	Rate of the Reaction at 240 nm ($r \times 10^{-3}$) mole / L min [$r \pm 0.5$]	Quantum Efficiency
5	2.21	0.55
10	4.56	0.55
15	6.95	0.55
20	9.27	0.55
25	11.86	0.55

3.3 The quantum efficiency

The quantum efficiency of the photoreaction of 5MT and BP has been determined using potassium ferrioxalate actinometer under various initial concentrations of 5MT. The plot of ϕ value vs. initial concentration of 5MT (**Figure 5(A)**) shows a straight line with positive slope suggesting dependence of quantum efficiency on the initial concentration of 5MT.

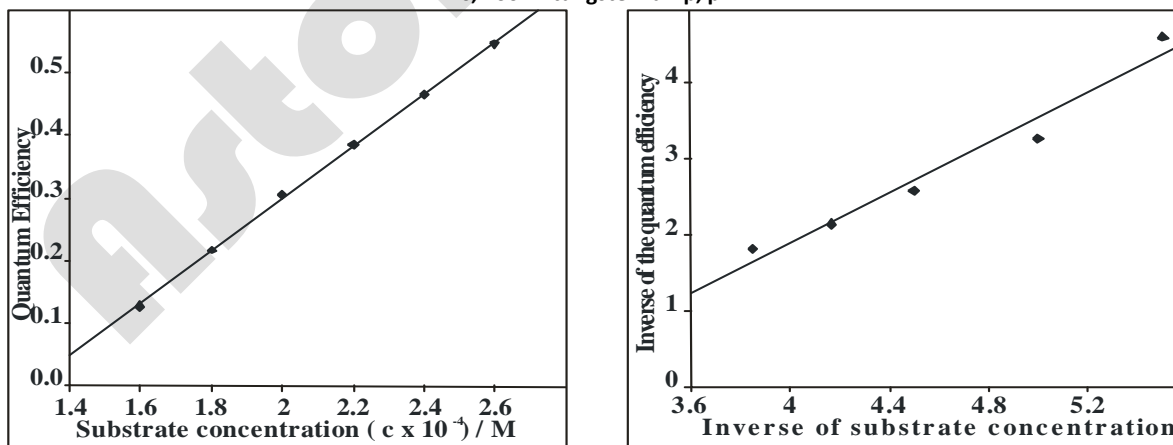
$$\phi_{Prod} = \frac{k_2 FG [5-MT]}{k_d + k_2 [5-MT]} \text{----- (1)}$$

$$\frac{1}{\phi_{Prod}} = \frac{1}{FG} + \frac{k_d}{k_2 FG [5-MT]} \text{----- (2)}$$

Where $F = \frac{k_p}{k_p + k_e}$ and $G = \frac{k_2}{k_{isc} + k_{sd}}$

Equation 2 represents the dependence of the inverse of the quantum efficiency on the inverse of the concentration of the substrate. As the concentration of 5MT increases, the plot of the inverse of the quantum efficiency Vs inverse of the concentration of the substrate (**Figure 5(B)**) shows linearity with positive slope indicating that the dipole-dipole energy transfer from triplet excited state of BP to ground state of 5MT. No exciplex formation takes place during this photosensitized reaction [10]. The photo reaction product formation is a monophotonic process as the quantum efficiency does not change with increase in light intensity.

Figure 5: Plot of (A) quantum efficiency Vs substrate concentration (B) inverse of the quantum efficiency Vs inverse of the substrate concentration at 240 nm, 5MT: 1.6×10^{-4} mol L⁻¹ to 2.6×10^{-4} mol L⁻¹, BP: 1×10^{-4} mol L⁻¹, time interval: 25 mins, 100 W tungsten lamp, pH 11.



3.4 Identification of the photo product

The reaction mixture after exposure to the visible radiation for 175 mins was analyzed for the reaction product, showing the absence of organic compound. The test for S²⁻ and SCN⁻ was found negative with lead acetate and FeCl₃ solution.

3.4.1 Test for the SO₄²⁻ ion

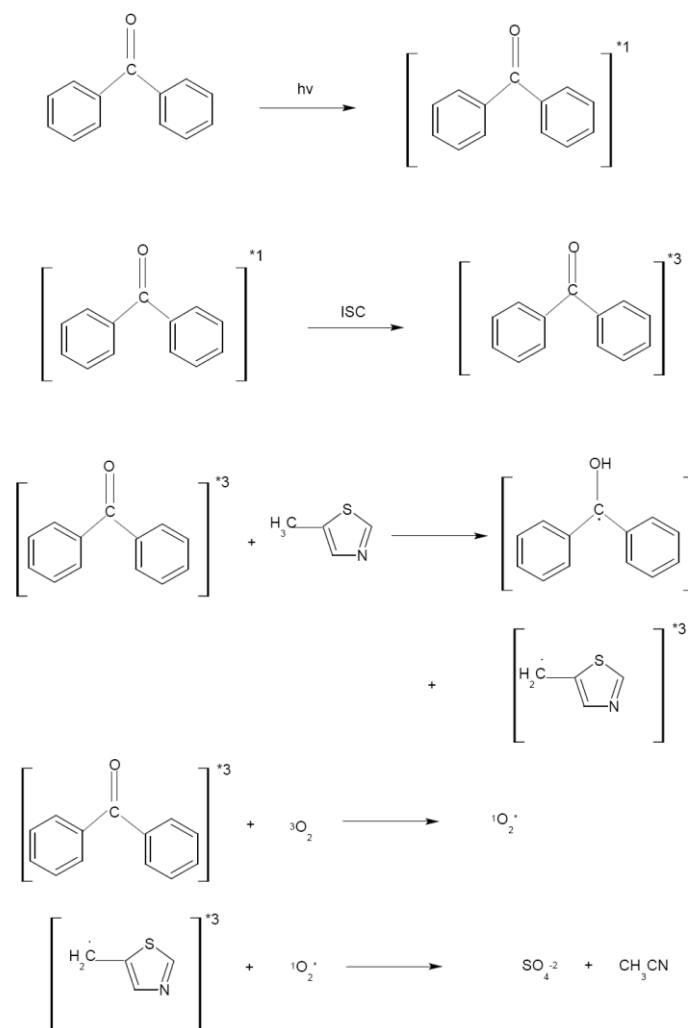
The reaction mixture was further tested for SO_4^{2-} ion with BaCl_2 and lead acetate solution which gave white precipitation. The triplet excited state molecule of 5MT undergoes decomposition to give sulphate as a photoproduct.

3.5 Mechanism

Aromatic ketone, benzophenone absorbs visible radiation and undergoes rapid intersystem crossing of the $n \rightarrow \pi^*$ singlet excited state to an energetically close $\pi \rightarrow \pi^*$ triplet state. The methyl substituted thiazole has absorbance below 400 nm and do not absorb visible light and are photo stable. The photosensitized reactions of 5MT with BP involve both the proton abstraction and photooxygenation reaction. The reaction follows the Type I photooxygenation reaction mechanism in which the sensitizer triplet state ($3S^*$) interacts with a substrate (XH), which gives rise to a free radical, by electron-transfer or hydrogen-transfer mechanisms. The free radicals produced react with singlet oxygen to regenerate the sensitizer to ground state and to form the photoproduct.

The triplet excited state of BP acts as proton abstractor and abstract proton from the CH_3 of the methyl thiazole and forms the methylene thiazole free radical in the triplet excited state and the BP molecule comes back to the ground state. The excited methylene thiazole free radical undergoes photooxygenation by singlet oxygen and gives sulphate and alkylcyanide as a photoproduct on ring cleavage. The plot of the inverse of the quantum efficiency versus inverse of the concentration of the substrate suggests that photoproduct is formed from the triplet excited state of methyl substituted thiazole and no exciplex formation takes place during the photoreaction.

Scheme 1: Mechanism of 5MT degradation.



4. Conclusion

The photosensitized reaction of 5MT with BP is used to mineralize 5MT to less toxic ions by dipole-dipole energy transfer mechanism. The irradiation of BP with visible light excites it to singlet excited state which gives triplet excited state on ISC. The triplet excited state of BP acts as proton abstractor and abstract proton from the CH₃ of the methyl thiazole and forms the methylene thiazole free radical in the triplet excited state and BP comes back to the ground state. The excited methylene substituted thiazole's free radical undergo photooxygenation by singlet molecule oxygen and gives sulphate and alkylcyanide as a photoproduct on ring cleavage. The first-order kinetic constant (apparent k) of the photodecomposition reaction of 5MT is independent of the concentration of 5MT and BP but dependent on the pH of the solution and light intensity. The plot of $1/\phi$ Vs $1/C$ suggests triplet-triplet energy transfer from the sensitizer to substrate without exciplex formation.

Competing Interests

None declared.

Authors' Contributions

MDD: Research work planning and practical work; ADD: Literature survey, manuscript preparation; UCP: Guidance throughout the research work.

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