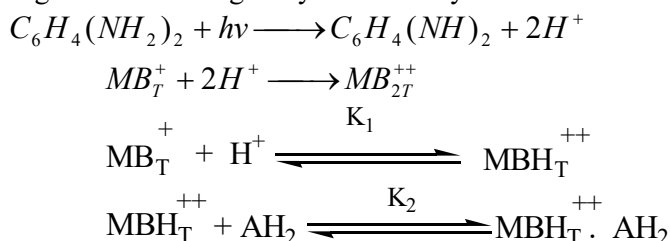


Photo Redox Kinetics and Mechanistic Study of Methylene Blue and Paraphenyldiamine

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Abstract

This article investigates the methylene blue (MB) dye reduction on a specially designed optical bench under the radiation of 656 nm through the oxidation of p-phenylenediamine (PPDA), an extreme sensitizer in a methanolic solvent. The oxidation of PPDA leads to the formation of polyaniline, a conductive polymer that is widely used in dye-sensitized applications and environmental remediation. Photoredox reaction studied on several acidic pH using acetate buffer and parameters (i) acidity (H_0) at the fixed concentration of dye (ii) various concentrations of PPDA, and (iii) temperature. The quantum yield was found to be a function of PPDA concentration, acidity, and temperature. It was concluded that a triplet transition state is involved in leuco dye formation and photo-oxidation of aromatic amine. It was also found that two equilibria were established between H^+ , dye, and PPDA (MB^+ , PPDA) and one form of triplet state of methylene blue with reductant PPDA. It was suggested that PPDA absorbed a photon of light and released 2 protons, which were abstracted by MB_T , resulting in the bleaching of dye or leuco dye formation.

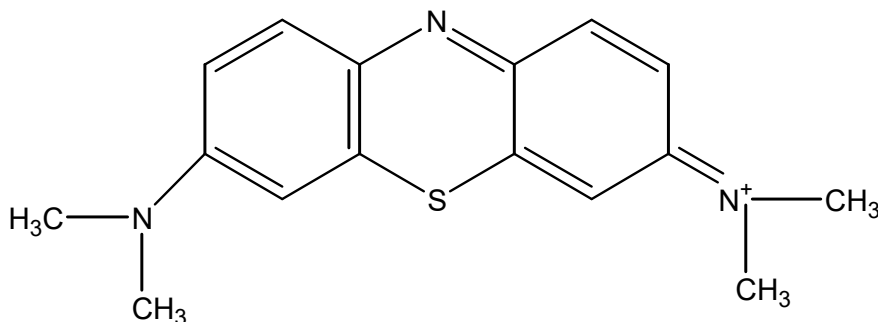


Keywords: methylene blue, photon, redox reaction, photo kinetics, quantum yield

1. INTRODUCTION

Photocatalytic reduction of dyes is an essential process in environmental remediation, chemical synthesis, and energy applications. Sunlight or UV light is used as an energy source to reduce dependence on harsh chemicals. Photocatalytic dye reduction helps in designing better photocatalysts for broader applications in environmental and energy-related fields [1, 2]. Methanol plays a significant role in the reduction of dyes, depending on the system and conditions. It acts as an electron donor in redox reactions, especially under catalytic or photochemical conditions oxidized to formaldehyde or formic acid while donating electrons for dye reduction [3]. It enhances the reduction of dyes by scavenging photogenerated holes, preventing charge recombination, and promoting electron transfer to the dye[4]. It increases the rate of dye reduction by providing a readily available source of electrons and affecting the solubility and interaction of dyes with reducing agents [5]. In wastewater treatment, methanol is sometimes used to assist in the photocatalytic or chemical degradation of dyes, helping in dye removal from industrial effluents. The dye reduction process is enhanced due to the increase in the availability of protons. Many dyes, especially azo dyes, undergo protonation in acidic media reduced to aromatic amines[6]. This makes them more susceptible to valuable reduction in the dye and pharmaceutical industries and controlled reduction without excessive degradation. Para-Phenyldiamine (PPDA) is an aromatic amine that plays a crucial role in dye reduction due to its strong electron-donating properties and redox activity as it donates electrons undergoes oxidation itself, facilitating the reduction of dyes, particularly azo dyes, by breaking their azo ($-N=N-$) bonds, forming quinonoid or polymeric species [7,8].

The most stable form of methylene blue [MB] is monochloride with molecular formula $C_{16}H_{18}ClN_3S \cdot 2H_2O$ having the IUPAC name of 3,7-bis-(dimethylamino)-phenothiazine-5-ium chloride. The structure of the singly protonated form is shown below:



This structure is in agreement with the structure of the thiazine dye given by Fischer [9], Bonneau *et al.* [10, 11] and Kikuchi *et al.* [12]. This form of methylene blue is found in the pH range 0.65 to 10.2. The leucodye (MBH_2) was formed by Obata *et al.* [13, 14] from photoreduction of MB. Formation of the leucodye (MBH_2) through photoreduction of the intermediate MBH was also reported by Matsumoto [15, 17] and Kato *et al.* [17]. Some important quantitative and qualitative investigations were made by Atherton and Harriman [18], Fahimuddin [19, 20], Fahimuddin *et al.* [21, 22], Jain *et al.* [23], Liu *et al.* [24], Fahimuddin and Hasnain [25], Kundu *et al.* [26] and Fahimuddin *et al.* [27-34]. Guler and coworkers [35, 36] studied the photoreduction of methylene blue and thionine by water. They found that photoreduction of MB proceeds in red light with only water available as a reducing agent. Although many investigators have studied the photochemical behavior of excited dye molecules [15, 37-42], little attention was devoted to kinetic studies of the photochemical reactions of thionine and methylene blue in the presence of organic reductants.

Chacko *et al.* [43] narrate the different enzymatic mechanisms in the reduction of azo dyes. Ganapuram *et al.* [44] synthesized stable gold nanoparticles (AuNPs) using *salmalia malabarica* gum as both a reducing and capping agent. The synthesized AuNPs exhibited good catalytic properties in the reduction of methylene blue and Congo red. Degradation of Brilliant Green (BG) dye has been studied using a Fenton reagent in the dark environment by Rao *et al.* [45]. They found that the Intensity of dye color was pH dependent with maximum absorbance at pH 6, and N-de-alkylation caused dye decomposition.

In the present work, Para-phenylenediamine (PPD) and methylene blue dye were used for studying the photo redox reaction on a specially designed optical bench at 656nm to monitor the decolorization of methylene blue at several kinetics parameters followed by the determination of quantum yield.

2. MATERIALS AND METHODS

An optical bench housed in a dark room was constructed (Fig. 1). A high-pressure mercury lamp (ME/D compact Mazda box type) was used as a light source. A Kodak written filter (no 15) was used to obtain monochromatic light at 656 nm. A parallel beam of light was received through lenses L_1 , L_2 , and L_3 . A red light of 656 nm was used to pass this parallel beam through the filter. Photocells P_1 and P_2 measured the Intensity of light (I_0), and the signals of photocells were obtained through galvanometers (G_1 and G_2). A plane reflecting glass R was used for the reflection of light to a reference photocell P_2 , and the remaining fraction of light was passed through the reaction cell (C) as shown in Figure 2. This reaction cell was an upgraded and modified version to the cell previously used by Atkinson and Di [46], Sawkar [47], and Ahmed [48].

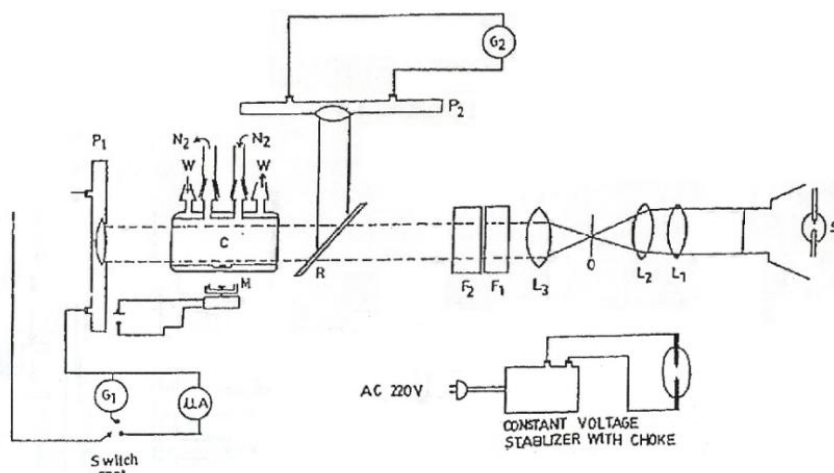


Figure 1: Optical Bench in Photochemical Research Lab

The reaction solution was bubbled with oxygen-free nitrogen through a series of dreschel bottles as described by Feiser [49]. Chemicals such as methylene blue, paraphenyldiamne, hydrochloric acid, sodium hydroxide, sodium acetate, and oxalic acid used were of E. Merck, Germany. Extra pure methanol (Merck) was used after re-distillation. Nitrogen (N_2) gas was manufactured by Pakistan Oxygen Ltd. (98.8%). The stock solutions of methylene blue were stored in well-stoppered polyethylene bottles as suggested by Sawkar [47]. An optical method described earlier Fahimuddin [19] was adopted to determine the acidity of the solution.

The mercury mazda lamp was turned on for 30 minutes before the process began. Known amounts of PPDA and buffer solution in methanol were pipetted out into the reaction cell. Oxygen-free nitrogen was bubbled for 30 minutes before irradiation. The photocell responses were observed without the cell in the light beam (D_0), with the cell containing solvent (D_m) and the cell containing the reaction solution (D_{nt}) under continuous irradiation. The quantum yield of the photoreduction of methylene blue was determined by using the following equation:

$$\log \left(\frac{D_m - D_{nt}}{D_{nt}} \right) = \frac{I_0(1-\alpha)\varepsilon^* \phi L t}{2.303 V} + \log \frac{D_m - D_{ni}}{D_{ni}}$$

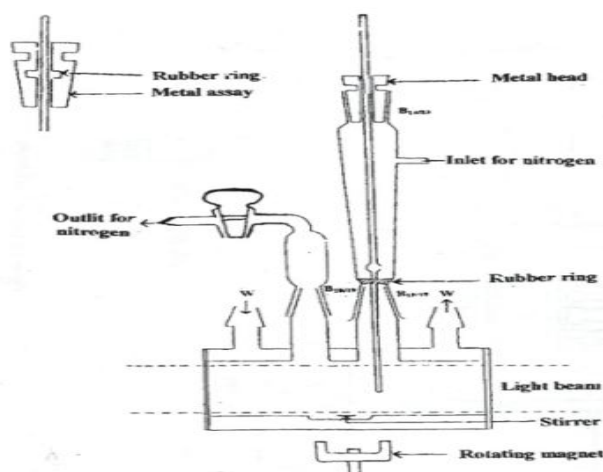


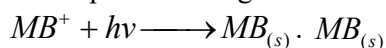
Figure 2: Arrangement of reaction cell.

where D_{ni} represents the photocell deflection for solution in the cell at zero time, α , the fraction of light lost at each window, ε^* , the molar absorption coefficient for methylene blue in absolute methanol at 656 nm (taken as $5.35 \times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) L , the length of the path traveled by the beam (7.0 cm) and V , the volume of the solution (0.025 dm^3). The quantum yield (ϕ) was calculated from the slope of the above equation.

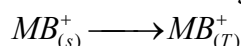
$$\text{i.e. } \phi = \frac{2.303 V}{I_0(1-\alpha)\varepsilon^* L} \times \text{slope}$$

3. RESULTS AND DISCUSSION

The reaction between methylene blue and paraphenyldiamine in the presence of acetate buffer has been studied at 656 nm in absolute methanol on a specially designed optical bench. Investigation showed that methylene blue became excited into a singlet transition state after the absorption of photons of light.

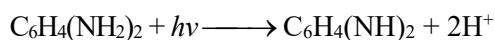


may convert into ground state dye by emission of radiation or change into triplet excited state by inter-system crossing,

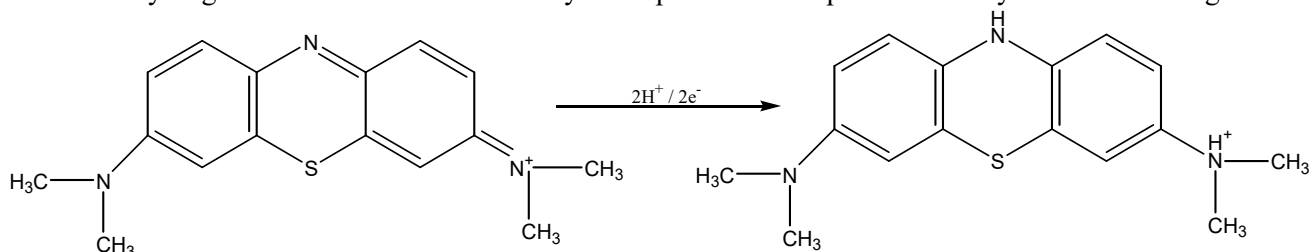


which has lifetime of $3.2 \mu\text{s}$, as earlier calculated by Wildes [50].

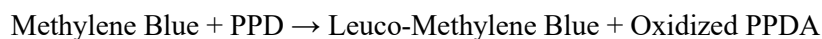
The primary photo-fragmentation process of aromatic amines does occur to a certain extent, especially at elevated temperatures. Aromatic amines are more photostable since a radiative emission process can dissipate the absorbed radiant energy:



The dissociated hydrogen from PPDA is abstracted by the triplet transient species of the dye in the following manner.



The dye will convert into the leuco dye by an oxidation-reduction process. MB exists in an oxidized form, which is deep blue. Para-phenylenediamine (PPDA) is a potent reducing agent that can reduce Methylene Blue (MB) through an electron transfer process, leading to a color change and transformation of MB into its leuco form MBH (LMB), which is colorless.



Photocatalytic dye reductions are enhanced by PPDA, often acting as a hole scavenger in semiconductor-based photocatalysis. It stabilizes intermediates during dye degradation, making the process more efficient. PPDA can donate

electrons, facilitating the reduction of dyes, particularly azo dyes, by breaking their azo ($-N=N-$) bonds. It undergoes oxidation itself while reducing dyes, forming quinonoid or polymeric species. The above reaction was investigated at different acidities, temperatures, and concentrations of reductants (PPDA) and dyes.

3.1. Photo redox reaction under varying paraphenyldiamine concentrations

The influence of the concentration of paraphenyldiamine in absolute methanol on quantum yield (ϕ) at 30 °C was studied at two different acidities. It was observed that quantum yield was increased with an increase in paraphenyldiamine concentration. The results are summarized in Table 1.

Table 1: Influence of Paraphenyldiamine Concentration on Quantum Yield

$10^4 [AH_2]$ mol dm ⁻³	$10^{10} I_0$ (Enist/s)	ϕ	$1/[AH_2] \times 10^{-3}$ (dm ³ .mol ⁻¹)	$1/\phi$
H₀ = 4.196				
8.0	3.96	0.275	1.250	3.64
16.0	3.79	0.349	0.625	2.87
32.0	3.83	0.442	0.313	2.26
40.0	3.71	0.449	0.250	2.23
48.0	3.19	0.548	0.208	1.82
60.0	3.87	0.579	0.167	1.73
H₀ = 8.090				
8.0	3.76	0.050	1.250	20.00
16.0	3.19	0.062	0.625	16.00
32.0	3.71	0.072	0.313	13.89
40.0	3.96	0.152	0.250	6.580
48.0	3.87	0.179	0.208	5.590
60.0	3.83	0.167	0.167	4.690

Results reported in Table 1 showed that the redox reaction is more favorable at low pH and directly related to the concentration of PPDA. The reciprocal of ϕ was plotted against $1/[AH_2]$ at both acidities and the plots were straight lines with positive slope (Fig 3). The values of ϕ at an infinite concentration of PPDA at acidities 4.196 and 8.090 are 0.60 and 0.20, respectively.

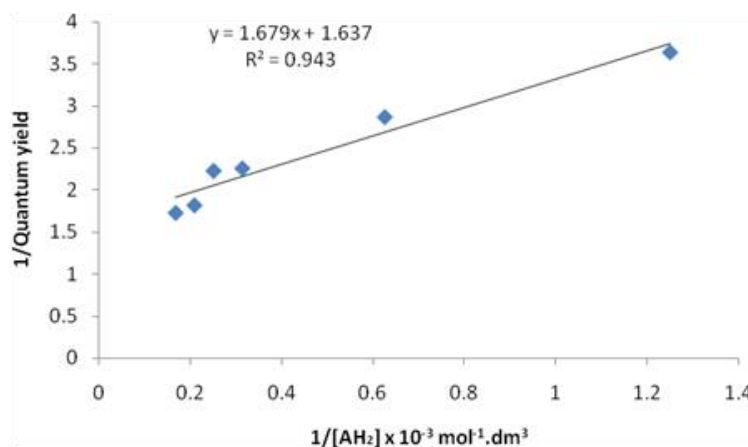


Figure 3: Plot of $1/\phi$ versus $1/[AH_2]$

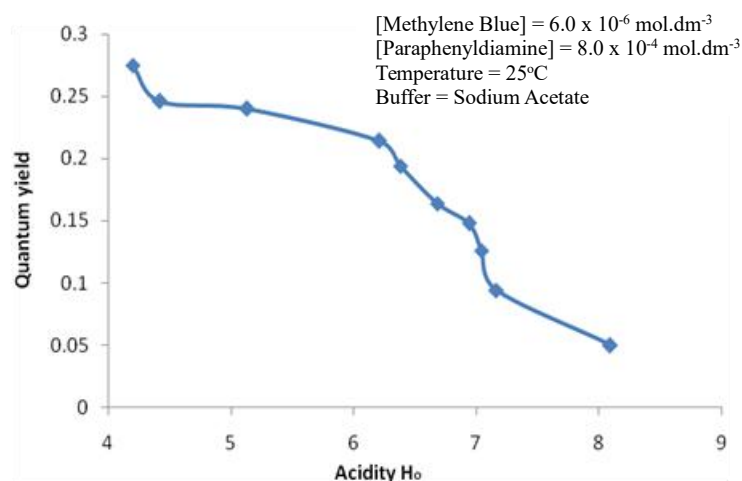
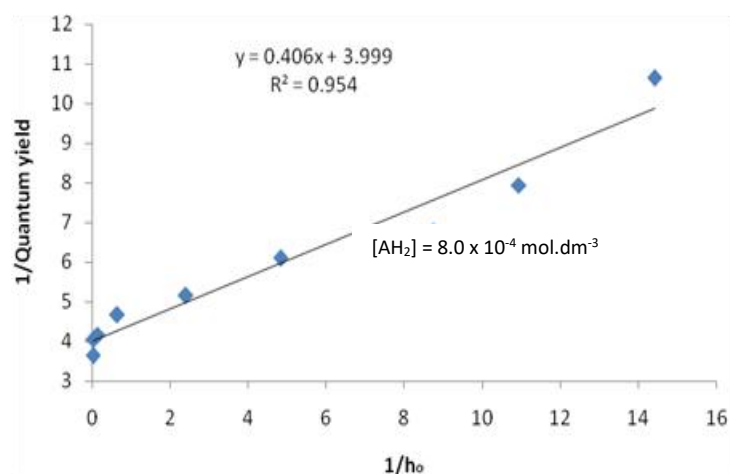
3.2. Photo redox reaction under varying acidities

The effect of the acidity on the solution quantum yield (ϕ) of the reaction mixture was observed using methanol as a solvent at two different concentrations of reductant (PPDA) at 30 °C. It was noted that the quantum yield decreased with the increase in acidity (H_0), which clearly showed that ϕ depends upon the pH of the medium. The results are tabulated in Table 2.

Table 2: Variation of Quantum Yield with Acidity

H_o	$10^{10}.I_o$ (Enist/s)	ϕ	$1/\phi$	$1/h_o \times 10^{-6}$ ($dm^3.mol^{-1}$)
$[AH_2] = 8.0 \times 10^{-4} mol.dm^{-3}$				
4.20	3.96	0.275	3.64	0.016
4.42	3.91	0.246	4.06	0.026
5.13	3.91	0.240	4.17	0.134
6.21	3.91	0.214	4.67	0.632
6.38	3.87	0.194	5.15	2.390
6.68	3.87	0.164	6.10	4.830
6.94	3.19	0.148	6.76	8.750
7.04	3.19	0.126	7.94	10.940
7.16	3.79	0.094	10.64	14.420
8.09	3.79	0.050	20.0	123.003
$[AH_2] = 4.0 \times 10^{-3} mol.dm^{-3}$				
4.20	3.71	0.449	2.227	0.016
4.42	3.71	0.397	2.519	0.026
5.13	3.75	0.242	4.132	0.134
6.21	3.75	0.197	5.076	1.632
6.38	3.19	0.180	5.556	2.390
6.68	3.19	0.164	6.098	4.830
6.94	3.96	0.158	6.329	8.750
7.04	3.96	0.142	7.042	10.940
7.16	3.71	0.121	8.264	14.420
8.09	3.96	0.082	12.195	123.033

The plot of ϕ versus H_o for methylene blue with PPDA is shown in Figure 4. The plot of the reciprocal of ϕ versus $1/h_o$ obtained is a straight line as shown in Figure 5. The variation of $(\phi_1 - \phi)/(\phi - \phi_2)$ with $1/h_o$ was also studied and the graph of $(\phi_1 - \phi)/(\phi - \phi_2)$ versus $1/h_o$ is shown in Figure 6. Here ϕ_1 and ϕ_2 are the quantum yields at extreme values of low and high acidities, respectively. This plot is a straight line passing through the origin.

**Figure 4:** Plot of ϕ versus H_o **Figure 5:** Plot of $1/\phi$ versus $1/h_o$.

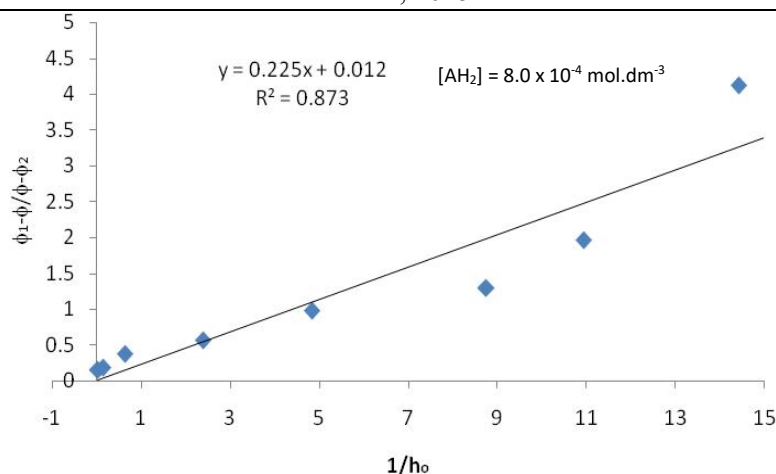


Figure 6: Plot of $\phi_1 - \phi / \phi - \phi_2$ versus $1/h_0$.

The influence of methylene blue concentration on quantum yield was also studied using absolute methanol as a solvent at a constant temperature of 30 ± 0.1 °C. The acidity of the reacting solution was kept constant as $H_0 = 8.09$. It was observed that quantum yield did not vary with dye [MB] concentration. The concentrations of MB were in the range of $6 - 8 \times 10^{-6}$ mol.dm⁻³ and the value of ϕ was constant at 0.098.

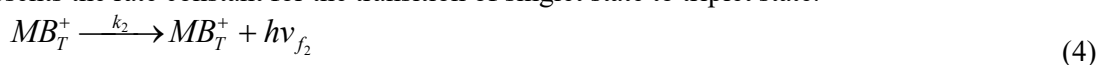
In view of the above discussion a general mechanism is proposed.



where I_a is absorbed photons.



where k_1 represents the rate constant for the transition of singlet state to triplet state.



where k_2 refers to the rate constant for the conversion of triplet state to unexcited methylene blue cation with phosphorescence.

The maximum chances maintenance of the triplet state is that it quickly associates with hydrogen ion with a lifetime of 3.2 μ s establishing equilibrium:



$$K_1 = \frac{[MBH_T^{++}]}{[MB_T^+][H^+]} \quad (6)$$

Quenching of the singly charged triplet state to ground state of methylene blue cation by the reductant PPDA [AH_2] is possible as:



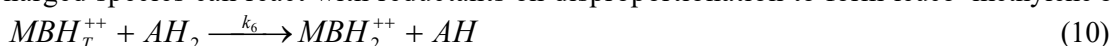
The reaction of the singly charged triplet species with the reductant PPDA to form semi-reduced methylene blue is represented as follows:



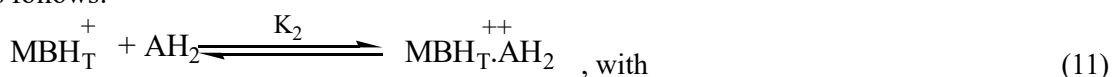
The singly charged triplet species may also deactivate to ground state dye by intersystem crossing as follow:



The doubly charged species can react with reductants on disproportionation to form leuco- methylene blue:

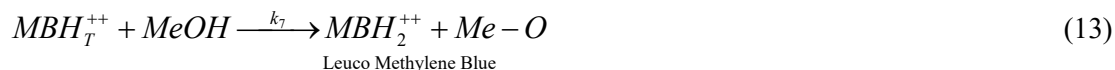


The doubly charged species on association with reductant can also establish an equilibrium with the formation of complex as follows:



$$K_2 = \frac{[MBH_T^{++} \cdot AH]}{[MBH_T^{++}][AH_2]} \quad (12)$$

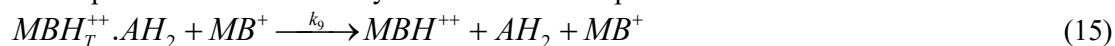
The semi-reduced dye i.e: MBH_T^{++} is also supposed to react with solvent molecule as follows:



The complex found in equation (11) losses its energy by internal conversion and finally dissociates to methylene blue as follows:



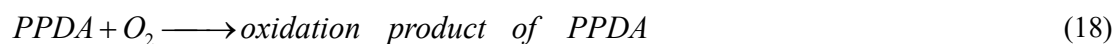
Quenching of the complex with unexcited methylene blue cation is represented as follows:



An oxidation reduction reaction can take place between unexcited dye and complex by transfer of electron also expressed as:



The free radical cation disappears as follows:



where k_1 to k_{10} refer to the rate constants of the respective processes as mentioned above.

Quantum yield can be defined as:

$$\phi = \frac{\text{disappearance of the dye}}{\text{no. of absorbed photons}} \quad (19)$$

$$\phi = \frac{-d[MB^+]/dt}{[I_a]} \quad (20)$$

Now if we suppose that

$$\begin{aligned} [MB_T^+] &= x, & [MBH_{2T}^{++}] &= y, & [MBH_T^{++} \cdot AH_2] &= z, \\ [MBH^+] &= d, & [AH_2] &= l & \text{and} & [H^+] &= h_o \end{aligned} \quad (21)$$

$$\frac{-d[MBH^+]}{dt} = \frac{1}{2}[k_3xl + k_6yl + k_7yl + k_9zd] \quad (22)$$

$$\text{and } \alpha[I]_a = k_2x + k_3xl + k_4xl + k_5x + k_6yl + k_7y + k_8z + k_9z d \quad (23)$$

Now

$$\phi = \frac{\alpha[k_3xl + k_6yl + k_7y + k_9zd]}{2[x(k_2 + k_3l + k_4l + k_5) + (k_6l + k_7)y + (k_8 + k_9d)z]} \quad (24)$$

$$\frac{1}{\phi} = \frac{2}{\alpha} \left[1 + \frac{(k_2 + k_4 + k_5)x}{k_3xl + y(k_6l + k_7) + zk_9d} + \frac{zk_8}{k_3zl + y(k_6l + k_7) + zk_9d} \right] \quad (25)$$

Now from equations (21), (6) and (12) we have:

$$K_1 = \frac{y}{xh_o} \quad y = K_1xh_o \quad \text{and similarly} \quad z = K_1K_2xh_o l \quad (26)$$

Substituting the values of y and z in equation (25), we get:

$$\frac{1}{\phi} = \frac{2}{\alpha} \left[1 + \frac{(k_2 + k_5)}{[k_3 + K_1k_6h_o + K_1K_2h_ok_9d]l} + \frac{(k_4K_1K_2k_8h_o)}{k_3 + K_1k_6h_o + K_1K_2h_ok_9d} \right] \quad (27)$$

Equation (27) represents the relationship between the reciprocal of the quantum yield ($1/\phi$) and the reverse of the concentration of reductant ($1/l$) i.e: $1/[AH_2]$. The plot between $1/\phi$ and $1/l$ is a straight line having slope and intercept as defined below:

$$\begin{aligned} \text{Slope} &= \frac{2}{\alpha} \cdot \frac{(k_2 + k_5)}{(k_3 + K_1 k_6 h_o + K_1 K_2 h_o k_9 d)} \quad \text{and} \\ \text{Intercept} &= \frac{2}{\alpha} + \frac{2}{\alpha} \cdot \frac{(k_4 + K_1 K_2 k_8 h_o)}{(k_3 + k_6 h_o + K_1 K_2 h_o k_9 d)} \end{aligned} \quad (28)$$

The intercept shows the quantum yield at infinite concentration; therefore, the equation (27) can be written as:

$$\frac{1}{\phi} = \frac{1}{\phi_o} + \frac{2}{\alpha} \cdot \frac{(k_2 + k_5)}{[k_3 + K_1 k_6 h_o + K_1 K_2 h_o k_9 d]} \cdot \frac{1}{l} \quad (29)$$

At high h_o , $\phi = \phi_1$ and at low h_o , $\phi = \phi_2$

At high h_o , x is negligible, and y and z are the controlling terms:

$$\frac{\phi_1 - \phi}{\phi - \phi_2} = \frac{\phi_1}{\phi_2} \cdot \frac{(x k_3 l)}{[y(k_6 l + k_7) + z k_9 d]} \quad (30)$$

Substituting the values of x and z and neglecting k_7 , we get:

$$\frac{\phi_1 - \phi}{\phi - \phi_2} = \frac{\phi_1}{\phi_2} \cdot \frac{k_3}{K_1 (k_6 + K_2 k_9 d) h_o} \quad (31)$$

Equation (31) shows that the plot between $\frac{\phi_1 - \phi}{\phi - \phi_2}$ and $1/h_o$ is a straight line passing through the origin and having a slope of:

$$\frac{\phi_1}{\phi_2} = \frac{k_3}{K_1 (k_6 + K_2 k_9 d)}$$

From equation (27) and neglecting k_3 and k_7 , we have:

$$\frac{1}{\phi} = \frac{2}{\alpha} \left[\frac{(k_2 + k_5)}{K_1 h_o (k_6 + K_2 k_9 d) l} + \frac{k_6}{(k_6 + K_2 k_9 d)} + \frac{k_3 + k_4}{K_1 h_o (k_6 + K_2 k_9 d)} + \frac{k_8 + k_9 d}{k_6 + K_2 k_9 d} \right] \quad (32)$$

This equation shows the relationship of $\frac{1}{\phi}$ with $1/l$ and $1/h_o$.

The values of the intercepts and slopes of the plots of $\frac{1}{\phi}$ against $[l/AH_2]$ as shown in Figure (3) were evaluated and tabulated as follow:

Reductant	H_o	Intercept	Slope 10^3 mol.dm^{-3}
Paraphenyldiamine	4.196	1.64 ± 0.024	1.68 ± 0.024
	8.090	4.83 ± 0.46	13.50 ± 0.70

The value of the ratios of the various rate constants for the reaction of methylene blue with Paraphenyldiamine evaluated from equations (27-33) are summarized in Table 3 and discussed as follows:

The ratio $(k_3 + k_4) / k_3$ depends on the singly protonated triplet species of methylene blue MB. In the high acidity region, k_4 is controlled by quantum yield; k_4 is comparatively higher than k_3 in low acidity region.

$[k_6/k_6 + K_2 k_9 d]$ is the ratio of rate constants for the disproportionation process of the doubly charged triplet and the hydrogen transfer reaction for the quenching of the complex with unexcited methylene blue cation. It depends on the hydrogen transfer process and hence Paraphenyldiamine was more associated with doubly protonated triplet state.

Table 3: The values of the ratios of rate constants

Ratios	Reductant Paraphenyldiamine
$\frac{k_3 + k_4}{k_3}$	20.00 ± 0.65
$\frac{k_6}{(k_6 + K_2 k_9 d)}$	3.64 ± 0.42
$\frac{k_5}{k_6}$	13.5 ± 0.7
$\frac{k_5}{(k_6 + K_2 k_9 d) K_1} \times 10^5$	2.3 ± 0.87
$\frac{(k_2 + k_5)}{(k_6 + K_2 k_9 d) K_1} \times 10^3$	1.68 ± 0.024
$\frac{k_5}{(k_6 + K_2 k_9 d) K_1} \times 10^4$	2.17 ± 0.041
$\frac{k_5 + k_4}{(k_6 + K_2 k_9 d) K_1} \times 10^5$	2.87 ± 0.126
$\frac{(k_8 + k_9 d) K_2}{(k_6 + K_2 k_9 d) K_1}$	1.64 ± 0.024

k_5/k_6 is the ratio of the rate constants for the deactivation of singly charged triplet to cation by intersystem crossing and disproportionation of the doubly charged triplet by reaction of methylene blue with paraphenyldiamine.

$\frac{k_6}{[(k_6 + K_2 k_9 d) K_1]}$ depends on the nature of the reductant. It is the ratio of the rate constants for the quenching of singly charged triplet state to ground state by reductant and the formation of a doubly charged triplet and the complex.

$\frac{(k_2 + k_5)}{(k_6 + K_2 k_9 d) K_1}$ is the ratio of rate constants for the deactivation processes and doubly charged triplet with the complex (MBH⁺⁺.AH₂).

$\frac{k_5}{(k_6 + K_2 k_9 d) K_1}$ is the ratio of the rate constant for the deactivation process of singly charged triplet of methylene blue with disproportionation of doubly charged triplet with reductant and the quenching of complex with unexcited methylene blue. It was also observed that this ratio also depends upon the nature of the reductant.

$\frac{k_5 + k_4}{(k_6 + K_2 k_9 d) K_1}$ is concerned with singly protonated triplet species, doubly charged triplet and the quenching of the complex. In low acidity region, the quantum yield is usually due to k_4 .

$\frac{(k_8 + k_9 d)}{(k_6 + K_2 k_9 d) K_1}$ is the ratio of rate constants due to dissociation of complex and product formation by methylene blue with association. This ratio depends on the chemical nature of the reductant paraphenyldiamine which followed by association.

From our results $\frac{2}{\alpha} \cdot \frac{k_5}{(k_6 + K_2 k_9 d) K_1} = 2.17 \times 10^{-4}$, the triplet quantum yield (α) is 0.45 and the dye

concentration is 10^{-6} mol.dm⁻³. The value of K_1 can be determined as 10^{-2} and the value of k_5 was given by Kayser & Young [43] as 7.0×10^6 (dm³/mol.s) for diethylamine. Hence $K_2.k_9 \cong 10^{19}$ (dm³/mol.s). The value of k_9 was reported earlier by Kayser & Young [49] as $k_9 \cong 10^{10}$ (dm³/mol.s), so the value of K_2 can be determined as 10^9 .

A reasonable value was compared to the value of 1.8×10^9 as reported by Bonneau *et al.* [10] and Solar *et al.* [39].

The variation of quantum yield with temperature is summarized in Table 4. The presently determined values of rate constants and the literature values are summarized in Table 4.

Table 4: Variation of quantum yield with temperature

TEMPERATURE °C	25	30	35	40	45
ϕ	0.178	0.275	0.348	0.416	0.484
Temperature Coefficients	ϕ_{30}/ϕ_{25} 1.545	ϕ_{35}/ϕ_{30} 1.265	ϕ_{40}/ϕ_{35} 1.195	ϕ_{45}/ϕ_{40} 1.163	Average 1.29

$[H_0] = 4.196$

The plot of quantum yield (ϕ) against temperature as shown in Figure 7 is a straight line with a positive slope. The observed temperature coefficient of 1.29 was the same as reported by Chibisov *et al.* [50]. It was observed that reduction is more effective at high acidity. The association of the base decreases with rising temperature, so the value of association constants could be assumed to decrease as temperature increases.

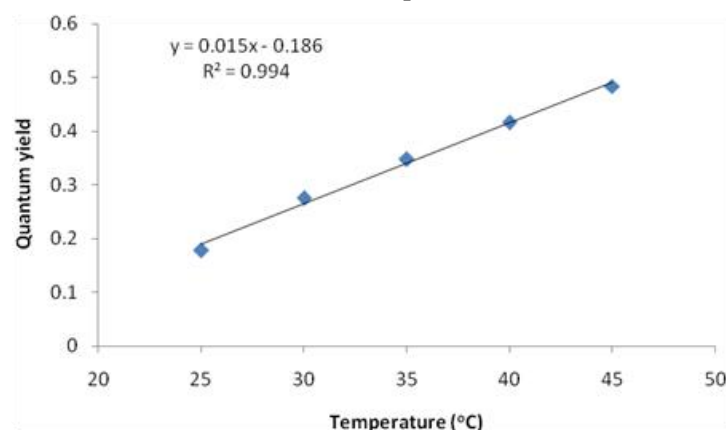


Figure 7: Plot of ϕ versus Temperature (°C)

CONCLUSION

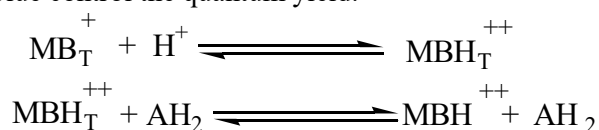
The photochemical reactions of methylene blue with paraphenyldiamine lead to the following conclusion:

There is no dependence of the quantum yield on the concentration of the dye.

The reduction of methylene blue depends on the concentration of the reductant i.e. paraphenyldiamine in absolute methanol.

It was observed that the quantum yield is a function of acidity.

Two excited species of methylene blue control the quantum yield.



It was observed that the photoreduction of methylene blue with paraphenyldiamine is very much influenced by the temperature.

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References

1. D. A. Bopape, B. Ntsendwana, & F. D. Mabasa, *A critical review. Heliyon.* (2024)
2. X. Zhang, S. Xiong, A. Sathiyaseelan, L. Zhang, Y. Lu, Y. Chen, & M.H. Wang *Chemosphere*, 143142 (2024).
3. W. Wu, L. Wen, L. Shen, R. Liang, R. Yuan, & L Wu, *Applied Catalysis B: Environmental*, 130, 163-167 (2013).
4. Q. Niu, X. Wang, J. Zhou, Y., Wang, & Y. Zhang, *Synthetic metals*, 160(21-22), 2381-2384. (2010).

5. N. A. Norhisamudin, N. Sabani, M. M. Shamimin, N. Juhari, S. Shaari, M. F. Ahmad, & N. Zakaria, In *Journal of Physics: Conference Series* (Vol. 1755, No. 1, p. 012024). IOP Publishing. **(2021, February)**
6. J. N. Chacon, J. McLearn, & R. S. Sinclair, *Photochemistry and photobiology*, 47(5), 647-656. **(1988)**.
7. H. M. Pinheiro, E. Touraud, O. Thomas, *Dyes and Pigments* ;61:121–39. **(2004)**
8. A. Meyer, & K. Fischer, *Environmental Sciences Europe*, 27(1), 1-16. **(2015)**
9. H. Fischer. *Zeitschrift fur Physikalische Chemie Neue Folge*. Bd. 43, 177-190 **(1964)**.
10. R. Bonneau, J. Faure, and J. J. Dubien, *J. Her. Bunssenges, Physical chemistry* 72(2), 263-266 **(1968)**.
11. R. Bonneau, J. Pereyre, and J. J. Dubien, *J. Mol. Photochem.* 6, 245-252 **(1974)**.
12. K. Kikuchi, H. Kokubun and M. Kikuchi. *Bullet. Chem. Soc. Japan*, 48, 1378-1381 **(1975)**.
13. H. Obata and M. Koizumi. *Bullet. Chem. Soc. Japan*, 30, 136-141 **(1957)**.
14. H. Obata, K. Kagasaka and M. Kozumi. *Bullet. Chem. Soc. Japan*, 32, 125- 132 **(1959)**.
15. S. Matsumoto, *Chem. Soc. Japan*, 35, 1860- 1866 **(1962)**.
16. S. Matsumoto. *Bullet. Chem. Soc. Japan*, 37, 499- 503 **(1964)**.
17. S. Kato, M. Morita, and M. Koizumi. *Bullet. Chem. Soc. Japan*, 37, 117-124 **(1964)**.
18. S. J Atherton and A. Harriman *The Arabian Journal for Science and Engineering* 21, 407- 424 **(1996)**.
19. F. Uddin. *European J. Org. Chem.*, 1345- 1351 **(2000)**.
20. F. Uddin, I.M. Adhami and M.A.K. Yousufzai. *J. Saudi Chem. Soc.* 2, 47- 59 **(1998)**.
21. F. Uddin, Q.Z. Hasnain and M.A.K. Yousufzai. *The Arabian Journal for Science and Engineering*, 26 (2A), 109-125 **(2001)**.
22. S. Jain, D. Geeta, J. Vardia and S.C. Ameta. *Int. J. Energy Research*, 23(1), 71-77 **(1999)**.
23. Y. Liu, S. Yamamoto, Y. Fujiyama and Y. Sueishi. *Physical Chemistry Chemical Physics*, 2, 2367-2371 **(2000)**.
24. F. Uddin and Q. Z. Hasnain. *Kuwait Journal of Science & Engineering*, 29(2), 67-85 **(2002)**.
25. S. Kundu, S. Kumar Ghosh, M. Mandal and T. Pal, *New Journal of Chemistry*, 27(3), 656-662 **(2003)**
26. F. Uddin, R. Saeed and Z. Khalid. *Turk. J. Chem.*, 28(3), 351-367 **(2004)**.
27. R. Azmat , S. Ahmed , S. Qureshi , F.V. Mohammed and F. Uddin, *J. App. Sci.*, 6(13), 2784-2788 **(2006)**
28. R. Azmat, N. Qamar, A. Saeed, F. Uddin, *Chin. J. Chem.*, 26, 631—634 **(2008)**
29. R. Azmat, F. Uddin, *Chin. J. Chem.*, 27, 1237-1243 **(2009)**
30. T. Ahmed, F. Uddin, R. Azmat, *Chin. J. Chem.*, 28, 748—754 **(2010)**
31. K. Ahmed, R. Azmat, F. Uddin, M.Q. *Chin. J. Chem.*, 29, 643—649 **(2011)**
32. T. Ahmed, Rafia Azmat & Fahim Uddin: *Journal of Environmental Chemistry and Ecotoxicology*, 4(8), 143-152 **(2012)**
33. M. Qadri, F. Uddin, & R. Azmat, *Pak. J. Chem.*, 4, 39-48 **(2014)**.
34. S. Guler and E.G. Micheal. *Photochem. and Photobiol.* 17, 179- 190 **(1973)**.
35. S. Guler and T. Aytekin. *Photochem. and Photobiol.* 10, 575- 580 **(1984)**.
36. J. Faure, J. R. Bonneau and J. J. Dubien. *Photochem. and Photobiol.* 6, 331- 339 **(1967)**.
37. H. E. A. Kramer, and A. Maute. *Photochem. and Photobiol.* 17, 413-423 **(1973)**.
38. S. Solar, W. Solar and N. Getoff. *Radiation Physical Chemistry*, 20, 165- 174 **(1982)**.
39. W. Vonnach and N. Getoff. *J. Photochemistry*, 23, 233-239 **(1983)**.
40. K. Viswanathan and P. Natarajan. *J. Photochem. and Photobiol.*, 95, 245-253 **(1996a)**.
41. K. Viswanathan and P. Natarajan. *J. Photochem. and Photobiol.*, 95, 255- 263 **(1996b)**.
42. T. Joshni. Chacko, K. Subramaniam. *Int.J.Environ.Sciences*, 1(6), 1250–1260 **(2011)**.
43. B. R. Ganapuram, A. Madhusudhan, D. Ramakrishna, A. Dasari, V. Maragoni, V. Guttena. *Int Nano Lett.*, 5, 215–222 **(2015)**.
44. Ch.V. Rao, A.S. Giri, V.V. Goud and A.K. *Trans. Faraday Soc.* 54, 1331- 1339 **(1958)**.
45. P. O. Sawkar. The kinetics of photochemical reduction of thiazine dyes by organic reducing agents. Ph.D. dissertation (University of London, London, U.K. **1960**)
46. M. G. Ahmed, 1963. Quantum efficiencies for some photochemical reactions of Thiazine dyes. Ph.D. dissertation (University of London, London, U.K, **1963**).
47. L. F. Feiser. *J. American Chem. Soc.* 46, 2639- 2647 **(1924)**.
48. P. D. Wildes, N.N. Lichtin, M.Z. Hofman, L. Andrews and H. Linschitz. *Photochem. and Photobiol.* 25, 21-25 **(1977)**.

49. R. H. Kayser and R. H. Young. *Photochem. and Photobiol.* 24(5), 403- 411 (**1976**).
50. A. K. Chibisov, G. I. Zakharova and G.V. Zacharova. *J. Inf. Rec. Mater*, 15(6), 395-421 (**1987**).

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