Photokinetic Study of Methylene Green with Dimethylamine

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ABSTRACT: The photokinetics of methylene green with dimethylamine in 50% aqueous isopropanol was studied. The quantum yield (ϕ) for the photochemical reaction of methylene green with dimethylamine was determined as a function of concentrations of methylene green, concentrations of reductant [AH_2], acidity [H_o] and temperature. The photochemical reduction was carried out in a special type of optical processor associated with a deoxygenating system, a temperature controlling unit and a magnetic stirring system. A monochromatic light of 657 nm wavelength was used for irradiation of oxygen free reaction solutions in a double walled reaction cell. The transmitted light was measured and recorded in terms of electrical signals with the help of a calibrated galvanometer. Acidities of the solutions were measured with the help of a spectrophotometer based on the Hammett acidity function [H_o]. It was observed that the quantum yield varies with reductant concentration [AH_2] and is independent of the concentration of methylene green at specific values of acidity and temperature. The results have been interpreted in terms of the reaction mechanism. The values of specific rate constants and ratios of rate constants were determined. It was found that 2 equilibria exists: i.e. one between the triplet state of methylene green with the proton and the protonated triplet state of methylene green [MGH_{2T}^{++}], and the other between the protonated triplet state of methylene green with reductants and associated the complex of methylene green [$MGH_{2T}^{++} AH_2$]. Thermodynamic parameters were also evaluated as a function of acidity.

Key words: Photokinetics, reduction, methylene green, dimethylamine, mechanism, thermodynamic parameters.
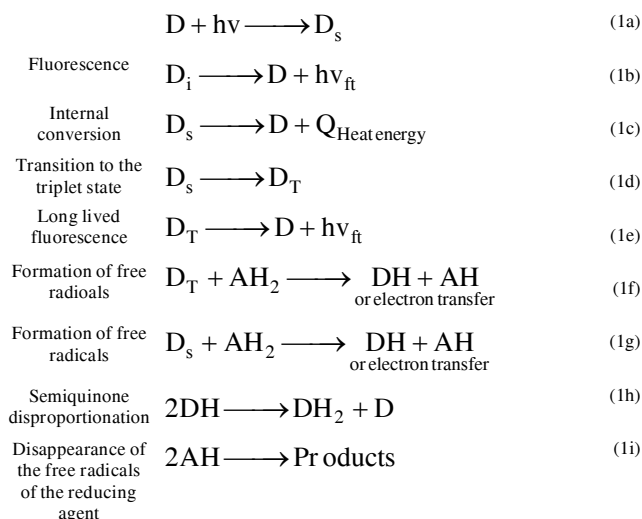
Introduction

Photochemical studies on methylene blue have been extensively investigated using variety of reducing agents and conditions [1-5]. Parker [6] has carried out flash photolysis studies using orange-red light. He found photo bleaching of methylene blue, very likely proceeding via a triplet of life time 20 m seconds. Koizumi *et al.* [7] studied the photoreduction of thiazine dyes such as new methylene blue, methylene green, toluidine blue and thionine. They attempted a kinetic treatment and found that in the borate buffer solution the reaction proceeds as of the first order with respect to the dye, while in the phosphate buffer solution the reaction is simple second order with respect to the dye. Thus the reaction mechanisms of the two cases are different. For methylene green, λ_{max} lies at 275 and 650 nm. The bleaching was

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moderately fast with a shift of the maximum from 650 to 610 ~ 620 nm. A new band appeared at 260 nm. The rate increased in order: plain aqueous solution < borate < phosphate Kulys et.al [8] studied the electrode action based on the effective reduction of oxidized L-lactate oxidase by reduced methylene green and rapid electrochemical mediator conversion. The spectrophotometric and viscometric analysis have been made to study the interaction of Methylene green in absolute and aqueous alcoholic systems at different temperatures. The aggregation of dye molecules and the effect of solvent on the nature of interaction have been studied through spectral analysis [9]. Uddin [10,11] studied the photochemical reduction of thionine and determined the quantum yield as a function of acidity and concentration of reductants and thionine.

The process of photoreduction is initially started by absorption of incident light. A dye molecule in the ground state is excited to another state of higher energy, a singlet

state. The fluorescence lifetime of this state is often about 10^{-8} seconds. There are several ways in which the dye molecule in this state can lose energy and various reviews have been published on the subject [5-12]. The following scheme gives the processes that are generally thought to be important in the photochemical reduction of dye [12].

$$D + hv \longrightarrow D_s \qquad (1a)$$

Fluorescence
$$D_i \longrightarrow D + hv_{ft} \qquad (1b)$$

Internal conversion
$$D_s \longrightarrow D + Q_{Heat\,energy} \qquad (1c)$$

Transition to the triplet state
$$D_s \longrightarrow D_T \qquad (1d)$$

Long lived fluorescence
$$D_T \longrightarrow D + hv_{ft} \qquad (1e)$$

Formation of free radioals
$$D_T + AH_2 \longrightarrow \underset{or\,electron\,transfer}{DH + AH} \qquad (1f)$$

Formation of free radicals
$$D_s + AH_2 \longrightarrow \underset{or\,electron\,transfer}{DH + AH} \qquad (1g)$$

Semiquinone disproportionation
$$2DH \longrightarrow DH_2 + D \qquad (1h)$$

Disappearance of the free radicals of the reducing agent
$$2AH \longrightarrow Pr\,oducts \qquad (1i)$$

where D = the dye, D_s = singlet state, D_T = the triplet state, DH = the semiquinone, DH_2 = the leucodye, AH_2 = the reducing agent.

Other mechanisms have been postulated e.g. the formation of a complex of the dye and reducing agent immediately on excitation of the dye was proposed [13-16]. The complex then gives the reaction products:

$$D_S. AH \rightarrow Products \quad (Ij)$$
$$D_T. AH \rightarrow Products \quad (Ik)$$
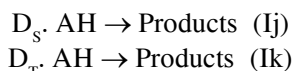
Many studies have been reported on complex and catalytic reactions [12-21]. Methylene green was studied electrochemically [8] and spectrophotometrically [9], but the published work for the subject of photochemical reactions of methylene green is scanty and no work was found for the determination of quantum yield for reduction of methylene green by organic reductants in aqueous alcoholic solutions.

The object of present work is to study the photokinetic reduction of methylene green with dimethylamine in aqueous isopropanol system. The quantum yield for reduction was observed as a function of concentration, temperature and acidity of the solutions. A mechanism was also proposed on the basis of results. Results were used to deduce the nature of steps involved in the photochemical reaction of methylene green with dimethylamine responsible for the variation in quantum yield in establishing the mechanism for the photoreduction process.

Experimental

All the glasswares used in the experiment were of Pyrex 'A' grade quality. Chemicals such as Isopropanol, acridine, dimethylamine, sodium hydroxide, sodium hydrosulphate, sodium anthraquinone-2-sulphate, lead acetate, sodium acetate, hydrochloric acid, sodium carbonate, sulphuric acid and oxalic acid were of E. Merck, Phenothiazine-5-ium, 3,7-bis (dimethyl-amino)-4-nitro-chloride commonly known as methylene green of analar grade manufactured by Fluka was used. 99.8% pure nitrogen gas supplied by Pakistan Oxygen Limited was used to remove the traces of oxygen. Freshly prepared double distilled water having a conductivity of 0.06×10^{-6} S/cm was used for the preparation of 50% aqueous isopropanol as solvent.

Optical Processor Arrangement

A special type of optical bench was designed for the optical measurements as described earlier [11], containing light source, monochromating system, double walled reaction cell, magnetic stirring system, photo detectors and Feiser's arrangement [7] for deoxygenation of reaction mixture. The light source (S) used for the reaction was a 250 Watt, 3 pin, 200-250 V per focus vapours high pressure mercury ME/D compact Mazda box type lamp (Code No. 94-0001). A mazda lamp manufactured by the General Electrical Company (GEC) of England was connected with 250 V constant voltage stabilizer (Hanovia) within $\pm$ 0.01 V. A parallel beam of light was obtained by passing the light through metal shield (H), convex lenses L_1, L_2 and L_3 and for obtaining a steady light beam from the hole in the metal plate (O). Filter (F) type Wratten filter by Kodak No. 608, of gelatin films about 0.1 mm thick was used to obtain monochromatic light of 657 nm. The monochromatic light was passed through the double walled reaction cell (C) with a capacity of 25 ml solution having 2 types of joints (B10/19). The reaction cell was attached to deoxygenated system for inlet and outlet oxygen free nitrogen and 2 joints (W) for the constant circulation of water attached to the thermostatic water bath type T-52 manufactured by Haake Karlsrühe, Germany to keep the temperature of reaction mixture constant with ± 0.1 °C as described earlier [14]. During the course of reaction, the reaction mixture was magnetically stirred by magnetic stirrer (M) fitted beneath the reaction cell and the stirrer was rotated by electric motor during the deoxygenating process to make the reaction mixture homogeneous. Light transmitted through the reaction cell and initial intensity of light with help of reflector (R)

showed response on Photocells (P_1) and (P_2) respectively. The photocells were used as photodetectors of cintel type QVA 39 connected in series with a 48 V dry cell. A Pye Universal shunt was connected to galvanometers (G_1 and G_2) S.S.6.45 and a 100 kW resistance to record the signals. All this arrangement was housed in a dark room.

Procedure

A known volume of reaction mixture was placed in the cell fitted with the nitrogen retractable bubbler and the outlet tap. Purified dry nitrogen was bubbled for 30 min. Then the bubbler was lifted up and the flow of nitrogen over the surface of the solution was maintained during the irradiation process. A monochromatic light of 657 nm was passed through the solution at fix temperature and the photocell responses were noted from the deflection on the scale of the galvanometer with no cell in the beam (D_o), with the cell containing solvent (D_m) and with the cell containing reaction solution (D_{nt}). The intensity of the light was measured from the ammeter. The intensity of light was measured by:

$$I_0 = 3.559 \times 10^{-6} \text{ x Einst/s} \qquad ...(2)$$

$$x = x_2 - x_1 \qquad ...(3)$$

where x_1 and x_2 are the galvanometer reading when no light is striking the photocell and when the photocell is exposed to light respectively.

Results and Discussion

The photokinetic of chemical reaction between methylene green and dimethylamine was studied as a function of concentration of reductant, concentration of dye, temperature and acidity (H_o). Hydrogen ion activity was determined in terms of Hammett acidity function (H_o) using an optical method [4] by the following relation:

$$H_o = p K + \log \frac{d_1 - d}{d - d_2} \qquad ...(4)$$

where d_1, d_2 and d are the extinction of the indicator in extreme acidic, basic and intermediate acidity solution respectively and the pK value for aqueous acridine solution [4] was taken as 5.45 ± 0.05. The acidity range was selected as 3.94 to 7.31.

The values of molar extinction coefficient with respect to pH were determined for 1.0×10^{-6} mol.dm^{-3} methylene green in 50% aqueous isopropanol at pH 4.00 and 7.31 were 0.55×10^4 and 1.05×10^4 mol.dm^{-3}.cm^{-1} respectively and the value of λ_{max} was found to be 657

nm. It was observed that the value of molar absorption coefficient is relatively high in basic medium.

The rate of decay of methylene green was determined in terms of quantum yield (ϕ), which is defined as moles of dye molecules of reactants converted into product per unit Einstein of light absorbed [16] and was calculated by the following relation:

$$\frac{\in \varphi L I_o (1 - \alpha)}{V} t = \log\left(\frac{D_m - D_{nt}}{D_{nt}}\right) - \log\left(\frac{D_m - D_{ni}}{D_{ni}}\right)$$
$$...(5)$$

$$\log\left(\frac{D_m - D_{nt}}{D_{nt}}\right) = \frac{\in \varphi L I_o (1 - \alpha)}{V} t + \log\left(\frac{D_m - D_{ni}}{D_{ni}}\right)$$
$$...(6)$$

where D_{ni} is the deflection for the reaction mixture in the cell at initial conditions, μ is the fraction of light lost at each window, $\in$ is the molar absorption coefficient for methylene green solution in 50% aqueous isopropanol, L is the length of path travelled by the beam in the cell, i.e. the length of the cell is 6.0 cm, V is the volume of the solution i.e. 0.0250 dm^3, I_o is the initial intensity of the beam and $(1 - \propto)$ is the fraction of light transmitted through the window measured during the experiment. Equation 6 is a straight line and the slope of the plot of $(D_m - D_{nt}) / D_{nt}$ versus time was used to calculate the quantum yield. The representative plot of $(D_m - D_{nt}) / D_{nt}$ versus time for the photochemical reduction of methylene green with dimethylamine at acidity (H_o) = 4.00 is shown in Figure 1.
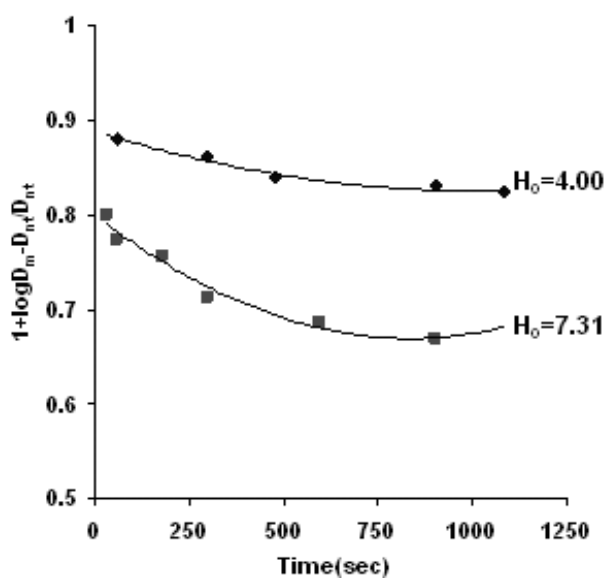

Figure 1: Plot of log $(D_m - D_{nt}) / D_{nt}$ versus time for photochemical reduction of methylene green with dimethylamine.

The photochemical reduction of methylene green with dimethylamine was studied on the basis of the variation in quantum yield under the influence of acidity (H_o) [5], concentration of reductant [DMA], concentration of dye [MG] and temperature are reported in Tables 1, 2, 3 and 4 respectively. The results show that the quantum yield increases by the increase in concentration of dimethylamine and also with the rise in temperature but independent of concentration of dye as no significant change was observed in quantum yield. It was also observed that quantum yield is much influenced by hydrogen ion as it plays a vital role in the reduction process. The curve obtained from the plot of quantum yield (ϕ) against acidity (H_o) for dimethylamine at concentration 5.0×10^{-2} mol.dm^{-3} is shown in Figure 2 indicate that the quantum yield are controlled by two excited species of methylene green which are predominent in the extreme regions of acidity. But from the point of inflexion, it shows that the concentration of the two excited species whether the singlet or the triplet state of the methylene green is involved in the effect of acidity. The singlet state could not be involved in the effect of acidity because the singlet state either converted to excited triplet state or deactivated to ground state by fluorescence process. Since fluorescence is assumed to take place from the conversion of the singlet state to the ground state, the effect of acidity must be dependent upon the triplet state.

Table 1
Effect of Acidity on Quantum Yield of Photochemical Reduction of Methylene Green with Dimethylamine

Acidity(H_o)	Quantum yield $(10.\varphi)$	
	$[AH_2] = 5.0x10^{-2}$ mol.dm^{-3}	$[AH_2] = 1.0x10^{-2}$ mol.dm^{-3}
3.94	0.544 ± 0.002	0.358 ± 0.002
4.00	0.398 ± 0.002	0.283 ± 0.003
4.33	0.322 ± 0.004	0.181 ± 0.008
5.44	0.304 ± 0.006	0.172 ± 0.008
6.46	0.206 ± 0.004	0.153 ± 0.002
6.90	0.171 ± 0.002	0.143 ± 0.003
7.31	0.146 ± 0.006	0.134 ± 0.006

Table 2
Effect of Concentration of Dimethylamine on Quantum Yield of Photochemical Reduction of Methylene Green

$10 . [AH_2]$ (mol.dm^{-3})	Quantum yield $(10.\varphi)$	
	$H_o = 4.00$	$H_o = 7.31$
0.05	0.112 ± 0.003	0.037 ± 0.005
0.10	0.126 ± 0.004	0.049 ± 0.001
0.20	0.132 ± 0.003	0.073 ± 0.002
0.50	0.197 ± 0.002	0.090 ± 0.002
1.00	0.283 ± 0.003	0.134 ± 0.001
5.00	0.398 ± 0.002	0.147 ± 0.003

Table 3
Effect of Concentration of Methylene Green on Quantum Yield of Photochemical Reduction of Methylene Green with Dimethylamine

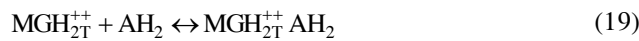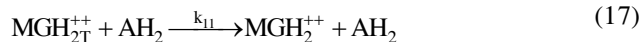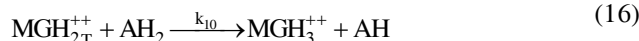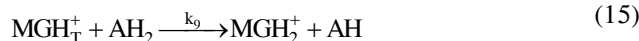| $10^{-6} . [MG]$ (mol.dm^{-3})	Quantum yield $(10 . \varphi)$
0.2	0.247 ± 0.003
0.4	0.246 ± 0.002
0.8	0.240 ± 0.001
1.2	0.235 ± 0.002
1.6	0.232 ± 0.002
2.0	0.227 ± 0.003
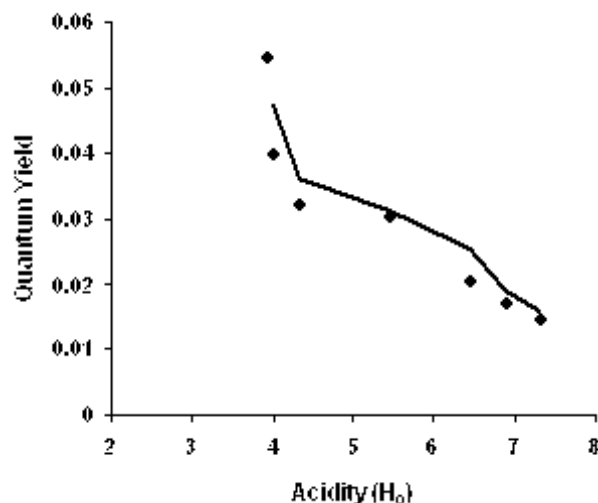
Figure 2: Effect of acidities (H_o) on quantum yield (ϕ) for photochemical reduction of methylene green with dimethylamine
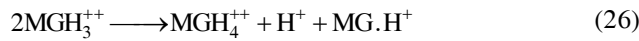
Table 4
Effect of Temperature on the Quantum Yield of Photochemical Reduction of Methylene Green with Dimethylamine

Reductant [AH_2]	Acidity (H_o)	Quantum yield $(10 . j)$ Temperature (K)				
		293	298	303	308	313
Dimethylamine	4.00	0.177 ± 0.003	0.208 ± 0.002	0.229 ± 0.002	0.281 ± 0.004	0.323 ± 0.002
	7.31	0.109 ± 0.003	0.147 ± 0.003	0.194 ± 0.001	0.234 ± 0.002	0.275 ± 0.006
				Temperature coefficients		
		$\varphi_{25}/\varphi_{20}$	$\varphi_{30}/\varphi_{25}$	$\varphi_{35}/\varphi_{30}$	$\varphi_{40}/\varphi_{35}$	Average
Dimethylamine	4.00	1.17	1.10	1.22	1.14	1.15 ± 0.05
	7.31	1.34	1.31	1.20	1.17	1.25 ± 0.08

Rate equations are derived on the basis of experimental data and the photokinetic of the reduction was studied. A general reaction mechanism of the photoch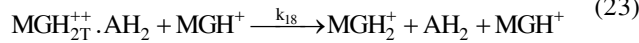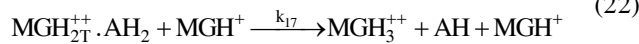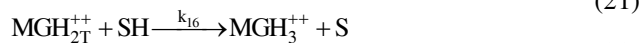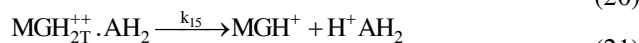emical reduction of methylene green with dimethylamine has been proposed on the basis of results obtained. The different steps of the reaction mechanism are as follows:
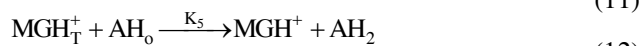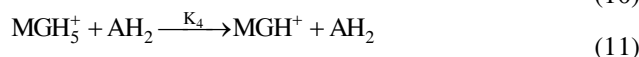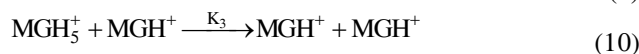
$$MGH^+ + h\nu \longrightarrow MGH_5^+ \qquad Rate = [I]_a \qquad (7)$$

$$MGH_5^+ \xrightarrow{K_1} MGH^+ + h\nu_f \qquad Rate = (1-\alpha)[I]_a \qquad (8)$$

$$MGH_5^+ \xrightarrow{K_2} MGH_T^+ \qquad Rate = \alpha[I] \qquad (9)$$

$$MGH_5^+ + MGH^+ \xrightarrow{K_3} MGH^+ + MGH^+ \qquad (10)$$

$$MGH_5^+ + AH_2 \xrightarrow{K_4} MGH^+ + AH_2 \qquad (11)$$

$$MGH_T^+ + AH_o \xrightarrow{K_5} MGH^+ + AH_2 \qquad (12)$$

$$MGH_T^+ \xrightarrow{K_6} MGH^+ \qquad (13)$$

$$MGH_T^+ + H^+ \leftrightarrow MGH_2^{++} \qquad (14)$$

$$K_1 = \frac{k_7}{k_s} = \frac{[MGH_2^{++}]}{[MGH_T^+][H^+]} \qquad (15)$$

$$MGH_T^+ + AH_2 \xrightarrow{k_9} MGH_2^+ + AH \qquad (16)$$

$$MGH_{2T}^{++} + AH_2 \xrightarrow{k_{10}} MGH_3^{++} + AH \qquad (17)$$

$$MGH_{2T}^{++} + AH_2 \xrightarrow{k_{11}} MGH_2^{++} + AH_2 \qquad (18)$$

$$MGH_{2T}^{++} \xrightarrow{k_{12}} MGH_2^{++} \qquad (19)$$

$$MGH_{2T}^{++} + AH_2 \leftrightarrow MGH_{2T}^{++} AH_2 \qquad (20)$$

$$K_2 = \frac{k_{13}}{k_{14}} = \frac{[MGH_{2T}^{++}.AH_2]}{[MGH_{2T}^{++}][AH_2]} \qquad (21)$$

$$MGH_{2T}^{++}.AH_2 \xrightarrow{k_{15}} MGH^+ + H^+ AH_2 \qquad (22)$$

$$MGH_{2T}^{++} + SH \xrightarrow{k_{16}} MGH_3^{++} + S \qquad (23)$$

$$MGH_{2T}^{++}.AH_2 + MGH^+ \xrightarrow{k_{17}} MGH_3^{++} + AH + MGH^+ \qquad (24)$$

$$MGH_{2T}^{++}.AH_2 + MGH^+ \xrightarrow{k_{18}} MGH_2^{++} + AH_2 + MGH^+ \qquad (25)$$

$$MGH_2^+ + H^+ \leftrightarrow MGH_3^{++} \qquad (26)$$

$$2MGH_2^+ \xrightarrow{k_d} MGH + MGH_3^{++} \qquad (27)$$

$$2MGH_3^{++} \longrightarrow MGH_4^{++} + H^+ + MG.H^+ \qquad (26)$$

$$AH + AH \longrightarrow Product \qquad (27)$$
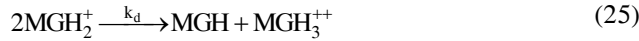
The kinetics of the photochemical reduction process were carried out by considering the various steps in the proposed mechanism. The rate of formation of experimental species is directly proportional to $[I]_a$, where $[I]_a$ is the quanta of light absorbed, which is calculated by adding rate equations of the proposed mechanism and could be written as:

$$\alpha[I]_a = [k_6[MGH_T^+][AH_2] + k_6[MGH_T^+] + k_9[MGH_T^+][AH_2] + \qquad (28)$$
$$k_{10}[MGH_{2T}^{++}][AH_2] + k_{11}[MGH_{2T}^{++}][AH_2] +$$
$$k_{12}[MGH_{2T}^{++}] + k_{15}[MGH_{2T}^{++}.AH_2] + k_{16}[MGH_{2T}^{++}] +$$
$$k_{17}[MGH_{2T}^{++}.AH_2][MGH^+] + k_{18}[MGH_{2T}^{++}.AH_2][MGH^+]]$$

Methylene green after reduction converts into semithionine and leucothionine. The rate of reduction of the process is equal to the rate of disappearance of methylene green.

Rate of disappearance of methylene green =

$$-\frac{d[MGH^+]}{dt}$$

$$-\frac{d[MGH^+]}{dt} = \frac{1}{2}[k_9]\big[MGH_T^+\big][AH_2] + k_{10}\big[MGH_{2T}^{++}\big][AH_2] +$$
$$k_{16}\big[MGH_{2T}^{++}\big] + k_{17}\big[MGH_{2T}^{++}.AH_2\big]\big[MGH^+\big] + \qquad (29)$$
$$k_{18}\big[MGH_{2T}^{++}.AH_2\big]\big[MGH^+\big]$$

Let

$$\big[MGH_T^+\big] = a, \big[MGH_{2T}^{++}\big] = b, \big[MGH_{2T}^{++}.AH_2\big] = c, \big[MGH^+\big] = d$$
$$[AH_2] = \ell \text{ and } \big[H^+\big] = h_o$$

Substituting these symbols in equations 28 and 29:

$$\alpha[I]_a = [k_5 a\ell + k_6{}^a + k_9 a\ell + k_{10}b\ell + k_{11}b\ell + \qquad ...(30)$$
$$k_{12}b + k_{15}c + k_{16}b + k_{17}cd + k_{18}cd$$

$$-\frac{d[MGH^+]}{dt} = \frac{1}{2}[k_9 a\ell + k_{10}b\ell + k_{16}b + k_{17}cd + k_{18}cd] \quad ...(31)$$

As k_{17} and k_{18} are constant values for quenching of the complex with unexcited dye cation and are equal, it can be represented only by k_{17} in equations 30 and 31:

$$\alpha[I]_a = [k_5 a\ell + k_6 a + k_9 a\ell + k_{10}b\ell + k_{11}b\ell + \qquad ...(32)$$
$$k_{12}b + k_{15}c + k_{16}b + k_{17}cd]$$

$$-\frac{d[MGH^+]}{dt} = \frac{1}{2}[k_9 a\ell + k_{10}b\ell + k_{16}b + k_{17}cd] \qquad ...(33)$$

The quantum yield (φ) of the photochemical reaction is defined as

$$\varphi = \frac{-d[MGH^+]/dt}{[I]_a} \qquad ...(34)$$

Substituting equations 32 and 33 in equation 34:

$$\varphi = \frac{\alpha}{2} \frac{[k_9 a\ell + k_{10} b\ell + k_{16} b + k_{17} cd]}{\begin{bmatrix} k_5 a\ell + k_6 a + k_9 a\ell + k_{10} b\ell + + k_{11} b\ell + \\ k_{12} b + k_{15} c + k_{16} b + k_{17} cd \end{bmatrix}} \quad ...(35)$$

According to mechanism steps 8 and 13:

$$K_1 = \frac{b}{ah_o} \qquad ...(36)$$

$$b = K_1 ah_o \qquad ...(37)$$

$$K_2 = \frac{c}{b\ell} \qquad ...(38)$$

$$c = K_2 b\ell \qquad ...(39)$$

Put the value of b:

$$c = K_2 K_1 a h_o \ell \qquad ...(40)$$

Substituting the values of 'b' and 'c' from equations 37 and 39 in equation 35:

$$\varphi = \frac{\alpha}{2} \frac{[k_9 a\ell + K_1 h_o [(k_{10}\ell + k_{16}) + K_2 k_{17}\ell d)]]}{\begin{bmatrix} k_5\ell + k_6 + k_9\ell + K_1 h_o + \begin{bmatrix} k_{10}\ell + k_{11}\ell + k_{12} + k_{16} \\ + K_2 k_{15}\ell + K_2 k_{17}\ell d \end{bmatrix} \end{bmatrix}} \quad ...(41)$$

At high h_o then $\varphi = \varphi_1$, where φ_1 is the quantum yield at high acidity.

At high acidity, the species $[MGH_T^+]$ is not supposed to be present; therefore the mechanism steps involving $[MGH_T^+]$ have been neglected and equation 32 is reduced to:

$$\varphi = \frac{\alpha}{2} \frac{\left[K_1 h_o \left(k_{10}\ell + k_{16} + K_2 k_{17}\ell d \right) \right]}{K_1 h_o \left(k_{10}\ell + k_{11}\ell + k_{12} + K_2 k_{15}\ell + K_2 k_{17}\ell d \right)} \quad (42)$$

When $\ell = 0$, equation 45 reduces to

$$\varphi_{(dvent)} = \frac{\alpha}{2} \frac{\left(k_{12} + k_{16} \right)}{k_{16}} \qquad ...(43)$$

At low h_o, $\varphi = \varphi_2$ and $\left| MGH_{2T}^{++} \right|, \left| MGH_{2T}^{++}.AH_2 \right|$, are not supposed to be present; thus

Equation 41 reduces to:

$$\varphi_2 = \frac{\alpha}{2} \frac{k_9\ell}{k_5\ell + k_6 + k_9\ell} \qquad ...(44)$$

where φ_2 is the quantum yield at low acidity.

$$\frac{\varphi_1 - \varphi}{\varphi - \varphi_2} = \frac{\varphi_1}{\varphi_2} \frac{k_9\ell}{K_1 h_o \left(k_{10}\ell + k_{16} + K_2 k_{17}\ell d \right)} \qquad ...(45)$$

Neglecting k_{16} from the denominator as due to the formation of activated complex the possibility of reacting with solvent (SH) can be neglected:

$$\frac{\varphi_1 - \varphi}{\varphi - \varphi_2} = \frac{\varphi_1}{\varphi_2} \frac{k_9}{K_1(k_{10} + K_2 k_{17} d)} \cdot \frac{1}{h_o} \qquad ...(46)$$

Equation 46 shows the relationship between $\varphi_1 - \varphi / \varphi - \varphi_2$ and $1/h_o$. The plot of this equation will be a straight line passing through the origin. A representative plot of $\varphi_1 - \varphi / \varphi - \varphi_2$ versus $1/h_o$ is shown in Figure 3.
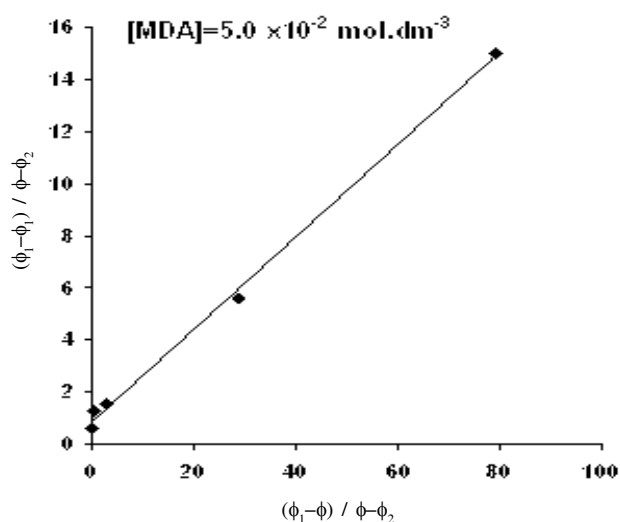

Figure 3: Plot of $(j_1 - j) / (j - j_2)$ versus $1/h_o$ for photochemical reduction of methylene green with dimethylamine.

The complexity of the ratios of rate constants can be removed by fixing some limitations and by neglecting less contributing rate constants, the simple ratios for expected rate constants can be obtained. Again referring to equation 42, and neglecting k_6, k_9 and k_{16}:

$$\frac{1}{\varphi} = \frac{2}{\alpha} \frac{k_{10}\ell + k_{11}\ell + k_{12} + K_2 k_{15}\ell + K_2 k_{17}\ell d}{k_{10}\ell + K_2 k_{17}\ell d} + \frac{2}{\alpha} \frac{k_5}{K_1(k_{10} + K_2 k_{17} d)} \cdot \frac{1}{h_o} \qquad ...(47)$$

Equation 47 shows the relationship between $1/\varphi$ and $1/h_o$, representing a straight line plot with slope

$$\frac{2}{\alpha}\frac{k_5}{K_1(k_{10}+K_2k_{17}d)} \text{ and intercept}$$

$$\frac{2}{\alpha}\frac{k_{10}\ell+k_{11}\ell+k_{12}+K_2k_{15}\ell+K_2k_{17}\ell d}{k_{10}\ell+K_2k_{17}\ell d}$$

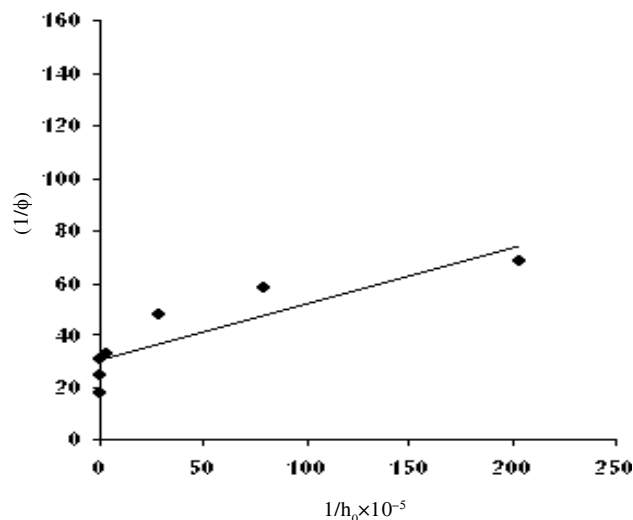**Figure 4:** Plot of reciprocal of quantum yield (1/φ) versus 1/h$_o$ for photochemical reduction of methylene green with dimethylamine.

A representative plot showing the effect of 1/φ versus 1/h$_o$ is shown in Figure 4.

At a constant concentration of reactant k_5 can be neglected as $\left|MGH_T^+\right|$ is not present; k_{10} and k_{11} can be neglected due to the formation of activated complex. If internal conversion processes (k_{12} and k_{15}) are neglected then:

$$\frac{1}{\varphi}=\frac{2}{\alpha}\frac{K_2k_{17}d}{k_{10}+K_2k_{17}d}+\frac{2}{\alpha}\frac{k_6}{K_1\left(k_{10}+K_2k_{17}d\right)}\cdot\frac{1}{h_o} \tag{48}$$

Equation 48 shows the relationship between $\dfrac{1}{\varphi}$ and $\dfrac{1}{h_o}$, representing a straight line plot with

$$\frac{2}{\alpha}\frac{k_6}{K_1(k_{10}+K_2k_{17}d)} \quad \text{slope and intercept}$$

$$\frac{2}{\alpha}\frac{K_2k_{17}d}{k_{10}+K_2k_{17}d}\text{ .}$$

The relation between quantum yield and reductant concentration is given by

$$\frac{1}{\varphi}=\frac{2}{\alpha}+\frac{2}{\alpha}\frac{k_{11}+K_2k_{15}}{k_{10}+K_2k_{17}d}+\frac{2}{\alpha}\frac{k_{12}}{k_{10}+K_2k_{17}d}\cdot\frac{1}{\ell} \tag{49}$$

This equation 49 shows the direct relation between 1/φ and 1/ℓ, i.e. 1 / [AH$_2$]. The plot is a straight line having a slope and intercept as follows:

$$\text{Slope}=\frac{2}{\alpha}\frac{k_{12}}{k_{10}+K_2k_{17}d}, \text{ Intercept}=\frac{2}{\alpha}+\frac{2}{\alpha}\frac{k_{11}+K_2k_{15}}{k_{10}+K_2k_{17}d}$$
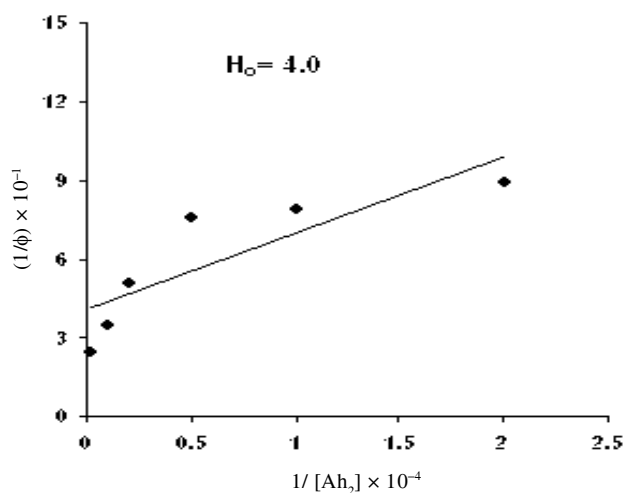

Figure 5: Plot of 1/φ versus 1/[AH$_2$] for photochemical reduction of methylene green with dimethylamine at H$_o$ = 4.00.

The intercept shows the quantum yield at infinite concentration and so equation 49 can be written as:

$$\frac{1}{\varphi}=\frac{1}{\phi_\infty}+\frac{2}{\alpha}\frac{k_{12}}{k_{10}+K_2k_{17}d}\cdot\frac{1}{\ell} \tag{50}$$

A representative plot showing the effect of reductant concentration on quantum yield as 1/φ versus 1/[AH$_2$] is shown in Figure 5.

The ratios of the rate constants for the proposed mechanism of reduction of methylene green with dimethylamine were calculated from the linear relations of mechanism steps. The values of the various ratios of rate constants and standard deviation are tabulated in Table 5.

Table 5
Ratios of Rate Constants of the Proposed Mechanism of Photochemical Reduction of Methylene Green with Dimethylamine

Ratios of rateConstants	Dimethyl-amine
$\dfrac{2}{\alpha}\dfrac{k_5+k_9}{k_9}$	79.066 ± 9
$\dfrac{2}{\alpha}\dfrac{k_6}{k_9}.10^3$	10.228 ± 0.1
$\dfrac{2}{\alpha}\dfrac{k_{12}}{k_{10}+K_2k_{17}d}.10^3$	2.913 ± 0.30
$\dfrac{2}{\alpha}\dfrac{k_{10}+k_{11}+k_{15}K_2+K_2k_{17}d}{k_{10}+K_2k_{17}d}$	40.721 ± 8
$\dfrac{2}{\alpha}\dfrac{k_5}{K_1(k_{10}+K_2k_{17}d)}.10^6$	2.135 ± 0.4
$\dfrac{2}{\alpha}\dfrac{k_6}{K_1(k_{10}+K_2k_{17}d)}.10^6$	1.582 ± 0.7
$\dfrac{2}{\alpha}\dfrac{K_2k_{17}d}{k_{10}+K_2k_{17}d}$	48.132 ± 6
(i) at low [AH$_2$]	3.116 ± 0.8
(ii) at high [AH$_2$]	1.906 ± 0.4
$\dfrac{k_5}{K_1k_{16}}.10^3$	5.432 ± 0.08
$\dfrac{k_6}{k_5k_9}.10^4$	1.293 ± 0.01
$\dfrac{k_{16}}{k_{10}+k_{11}+k_{15}K_2+K_2k_{17}d}.10^5$	7.154 ± 0.9

The correlation coefficients were also calculated, as the values as: $0.96<r<0.99$, indicate fair plots with excellent linearity. These ratios of the rate constants provide support to the proposed mechanism by giving an idea about the extent of the contribution of the protonated triplet excited state of methylene green in the reaction mechanism. The values of specific rate constant and equilibrium constant of certain steps in the proposed mechanism were also evaluated and are shown in Table 6. The mechanism shows that 2 equilibria are established: the first equilibrium exists at higher acidity where the triplet excited state combines with a hydrogen ion showing a reversible process:

$$MGH_T^+ + H^+ \leftrightarrow MGH_{2T}^{++} \qquad ...(14)$$
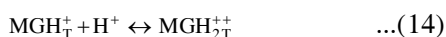
and the second when protonated triplet excited state is associated with a reductant molecule establishing an equilibrium state.

$$MGH_{2T}^{++} + AH_2 \leftrightarrow MGH_{2T}^{++}AH_2 \qquad (19)$$

The representative Figure 4 also represents the 2 equilibria, the first at high acidity and the second for the association of the protonated triplet excited state with reductant. The values of equilibrium constants K_1 and K_2 were obtained as 0.6×10^{-6} and 9.0×10^{14} mol^{-1}.dm^3, respectively, and tabulated in Table 6. These values are in accordance with the reported values as K_1 [18,19] of 10^{-6} mol^{-1}.dm^3 and K_2 [18,20] of 1.0×10^{14} mol^{-1}.dm^3.

Chemical kinetics and reaction rate theory help to elucidate reaction mechanism and determine the role of electronically excited molecules and free radicals formed in photo-dissociative processes. As the rate of reaction in terms of quantum yield also depend on concentration of reductant i.e. amines, the temperature dependence of experimental rate can be represented by the Arrhenius equation [21].

$$\varphi = A.\exp(-E_a/RT) \qquad ...(51)$$

Here φ is quantum yield in place of reaction rate constant, A is the pre-exponential factor or frequency factor, E_a is the experimental activation energy, T is the absolute temperature in °K, and R is the gas constant. The slope of the linear plot of quantum yield (log φ) versus 1/T gives the value of activation energy (E_a) for the photochemical reduction process.

The representative plot of quantum yield (log φ) versus 1/T is shown in Figure 6. It is observed that there is an increase in activation energy at low acidity ($H_o = 7.3$) as compared to high acidity ($H_o = 4.00$) relating to the higher value of quantum yield at high acidity. In terms of the transition state theory the rate of a photochemical reaction may be considered to be determined from the enthalpy and entropy change involved in the formation of activated complex. Enthalpy

Table 6
Specific Rate Constants of Mechanism of Photochemical Reduction of Methylene Green with Dimethylamine

Specific rate constant	Dimethylamine	
k_5 (mol^{-1} dm^3 s^{-1})	5.76x10^4	
k_9 (mol^{-1} dm^3 s^{-1})	1.90x10^6	
k_{11} (mol^{-1} dm^3 s^{-1})	1.07x10^{17}	
k_{12} (s^{-1})	7.92x10^{13}	
k_{15} (s^{-1})	1.15x10^3	

Equilibrium constant	Experimental	Literature
K_1 (mol^{-1} dm^3)	0.6x10^{-6}	10^{-6}
K_2 (mol^{-1} dm^3)	9.0x10^{14}	1.0x10^{14}

change (DH*) is related to the potential energy barrier for the reaction.

$$\Delta H^* = E_a - RT \qquad (52)$$

The larger value of enthalpy change shows the slower the rate of reaction.

In the interpretation of the pre-exponential factor (A):

$$A = \frac{K_B T}{h} \exp(\Delta S^*/R) \qquad ...(53)$$

by the transition state theory, a small factor indicates an improbable complex as the values obtained were negative from the above relation where K_B is Boltzmann's constant, h is Planck's constant.
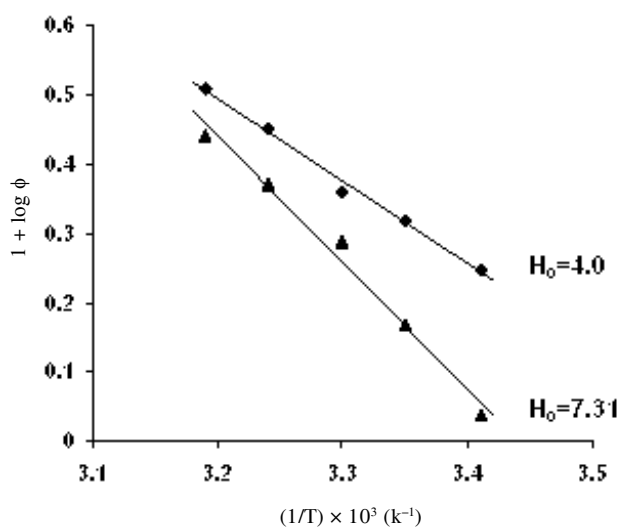

Figure 6: Plot of log ϕ versus 1/T for photochemical reduction of methylene green with dimethylamine

Free energy change of activation (ΔG^*) were evaluated by the relation:

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \qquad ...(54)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad ...(55)$$

where, ΔG^* is free energy change of activation, ΔH^* is the enthalpy change of action, ΔS^* is the entropy change of activation. The values for energy of activation, enthalpy change of activation, free energy change of activation, entropy change of activation are summarised in Table 7. It is observed that at low acidity there is an increase in the values of enthalpy change of activation, free energy change of activation and high negative values

of entropy change of activation. The higher value of E_a, ΔH and ΔG and negative value of ΔS led the conclusion to the formation of complex.

Conclusions

The quantum yield (φ) for the photochemical reaction of methylene green with dimethylamine in 50% aqueous isopropanol was determined as a function of concentration of methylene green, concentration of reductant [AH$_2$], acidity [H$_o$] and temperature. The results have been interpreted in terms of the reaction mechanism. The values of specific rate constants and ratios of rate constants were determined. The photochemical reduction of thionine with dimethylamine was also studied by Uddin et.al [15] and was found that the quantum yield was independent of concentration of thionine at a fixed value of concentration of reductant and acidity. The value of quantum yield (φ) for the photochemical reaction of methylene green with dimethylamine in 50% aqueous isopropanol was found to be 0.398 and 0.146 at acidity 4.0 and 7.3 respectively which are in accordance with the results reported by Uddin et al. [15] for thionine with dimethyamine as 0.286 and 0.146 and by Saeed et al. [14] for methylene green with methylamine as 0.336 and 0.122 at acidity 4.0 and 7.3 respectively. The decrease in quantum yield (φ) with increase in acidity led to the conclusion that the quantum yield (φ) of reduction of methylene green with dimethylamine in 50% aqueous isopropanol is a function of acidity and the plots between the quantum yield (φ) and acidity (H$_o$) are curved having sudden depression point at the region of H$_o$ 4.0 to 7.0, showing protolytic equilibrium of triplet state having transient region which controls the two processes: i.e. one between the triplet state of methylene green with the proton and the protonated triplet state of methylene green $[MGH_{2T}^{++}]$, and the other between the protonated triplet state of methylene green with reductants and associated the complex of methylene green $[MGH_{2T}^{++} AH_2]$.

$$MGH_T^+ + H^+ \rightleftharpoons MGH_{2T}^{++}$$

$$MGH_{2T}^{++} + AH_2 \rightleftharpoons MGH_{2T}^{++} AH_2$$
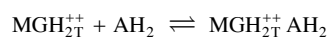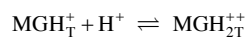
The values of equilibrium constants K_1 and K_2 were obtained as 0.6×10^{-6} and 9.0×10^{14} mol^{-1}.dm^{-3} which are in accordance to the previous work of photochemical reduction of methylene green with methylamine [14] as the values of K_1 and K_2 are 3.67×10^{-6} mol^{-1}.dm^3 and 5.07×10^{14} mol^{-1}.dm^3 respectively.

Table 7
Thermodynamic Parameters for Photochemical Reduction of Methylene Green with Dimethylamine at
298 k and at Different Acidities (H$_o$)

Acidity (H$_o$)	Thermodynamic Parameters			
	Energy of activation (E_a) (kJ mol^{-1})	Change in enthalpy of activation (ΔH) (kJ mol^{-1})	Change in free energy of activation (ΔG) (kJ mol^{-1})	Change in entropy of activation (ΔS) (J.K^{-1} mol^{-1})
4.00	22.649±1.4	20.172±0.08	106.155±2.2	-288.537±1.5
7.31	38.925±2.0	36.447±0.06	137.816±1.5	-340.164±0.2

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