

# The Kinetics of the Photochemical Reaction of Methylene Green with Methylamine and Ethylamine

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The photochemical reduction of methylene green with methylamine and ethylamine in 50% aqueous isopropanol was studied. 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  $[H_o]$ . The quantum yield ( $\varphi$ ) for the photochemical reaction of methylene green with methylamine and ethylamine was determined as a function of concentrations of methylene green, concentrations of reductants  $[AH_2]$ , acidity  $[H_o]$ , temperature and alkyl group associated with amine or the nature of the reductant. 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 for ethylamine were found to be relatively higher than those of methylamine, which shows that the reactivity of amines increases as the number of alkyl groups increased in amines. It was found that 2 equilibria exist: 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 the concentration of reductant, acidity and temperature.

**Key Words:** Photochemical reduction, methylene green, amines, kinetics, mechanism, thermodynamic parameters.

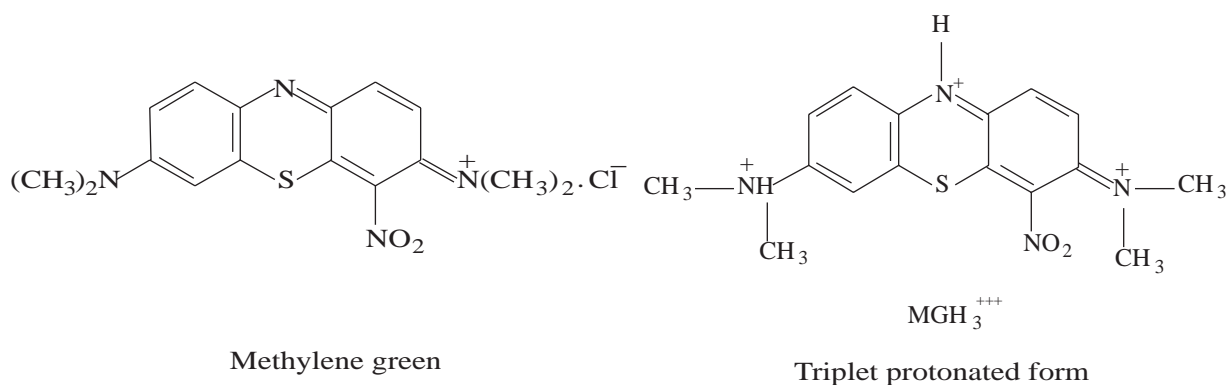
## Introduction

The literature provides knowledge of some fundamental information about thiazine dyes<sup>1-3</sup>. It concerns the effect of inhibitors, buffers, and reductants on photochemical reactions. It also reveals the mechanism of

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electron transfer in several photophysical and photochemical processes. The published work of photochemical reactions of thiazine dye is limited to the observations on thionine and methylene blue. Koizumi et al.<sup>4</sup> studied the photoreduction of thiazine dye such as new methylene blue, methylene green, toluidine blue and thionine. They studied kinetic treatment in different buffer media. Methylene blue photochemistry has been extensively investigated using a variety of reducing agents and conditions by several researchers<sup>5-16</sup>. Methylene green is a member of the thiazine dyes, and undergoes reduction by visible light with reductant in the presence of buffer solution. Acidity plays a significant role in the reduction of dye. The basic green, phenothiazine-5-ium, 3,7-bis (dimethyl amine)-4-nitro chloride is the stable form of methylene green<sup>9</sup>.



Methylene green was studied spectrophotometrically<sup>10</sup>, electrochemically and with cyclic voltammetry but kinetic studies of the photochemical reaction of methylene green are rare. The aim of the present work was to study the kinetics of the photochemical reduction of methylene green with methyl and ethylamines in terms of quantum yield.

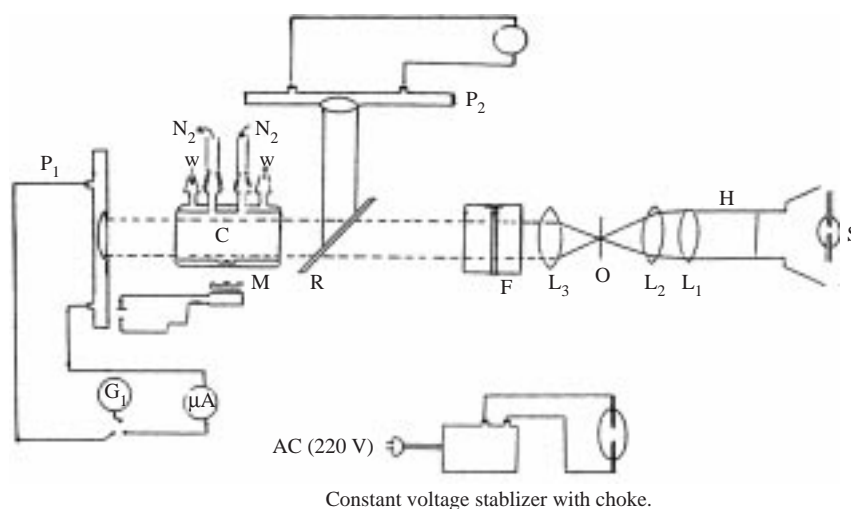
## Experimental

All the glasswares used in the experiment were of Pyrex 'A' grade quality. They were thoroughly washed and cleaned and then dried in an oven (W.T.C. binder, 7200, Tuttlinger/Germany Type E28 No. 89248) above 100 °C for several hours. A thermostatic water bath type T-52 manufactured by Haake Karlsruhe, Germany was used to maintain the temperature of reaction mixture constant throughout the experiment.

### Optical Processor Arrangement

A special type of apparatus was designed in the form of an optical bench as shown in Figure 1. The light source (S) used for the reaction was a 250 W, 3 pin, 200-250 V per focus vapours high pressure mercury ME/D compact Mazda box type lamp (Code No. 94-0001) manufactured by the General Electrical Company (GEC) of England. The voltage was kept constant and stabilised within 0.01 V using a 250 V constant voltage stabiliser by Hanovia. The optical system for obtaining a parallel beam (H) consists of a metal shield having a cylindrical metal tube about 8.0 cm in length and 5.0 cm in diameter. The monochromating system has lenses L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> for obtaining a steady light beam from the hole in the metal plate (O). Filter (F) type Wratten filter by Kodak No. 608, spectrum red, of gelatin films about 0.1 mm thick was used to obtain monochromatic light of 657 nm. There was also a double walled cell (C) of cylindrical shape with a capacity of 25 ml solution having 2 types of joints B10/19 for inlet and outlet oxygen free nitrogen and 2 joints (W)

for the constant circulation of water with  $\pm 0.1$  °C as shown in Figure 2. A magnetic stirrer (M) was fitted beneath the reaction cell and the stirrer was rotated by electric motor during the deoxygenating process to make the reaction mixture homogeneous. Deoxygenation was conducted by Feiser's method<sup>11</sup>. Photocells ( $P_1$  and  $P_2$ ) used as photodetectors were of cintel type QVA 39 connected in series with a 48 V dry cell, a Pye Universal shunt, galvanometers ( $G_1$  and  $G_2$ ) S.S.6.45 and a 100 kW resistance to record the signals. Photocell ( $P_1$ ) responds to the initial intensity of light reflected by the plain reflector (R) and the second photocell ( $P_2$ ) gave a response to the light transmitted through the reaction cell. All this arrangement was termed the optical processor as shown in Figure 1, and was housed in a dark room.



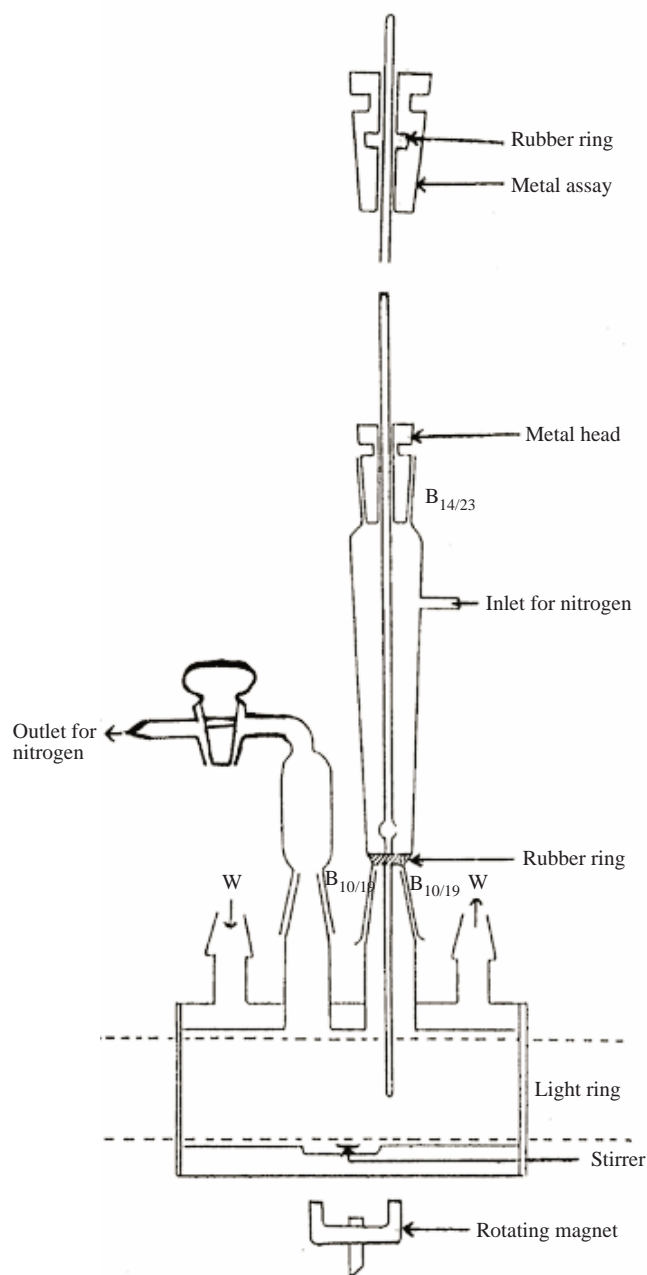
**Figure 1.** Arrangement of optical bench.

## Chemicals

Methylene green of analar grade manufactured by Fluka was used. Isopropanol, acridine, methylamine, ethylamine, sodium hydroxide, sodium hydrosulphate, sodium anthraquinone-2-sulphate, lead acetate, sodium acetate, hydrochloric acid, sodium carbonate, sulphuric acid and oxalic acid from E. Merck were used without further purification. Freshly prepared double distilled water having a conductivity of  $0.06 \times 10^{-6}$  S/cm was used for the preparation of 50% aqueous isopropanol as solvent; 99.8% pure nitrogen gas supplied by Pakistan Oxygen Limited was used.

## 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 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.



**Figure 2.** Arrangement of reaction cell.

Measurement of light intensity: The intensity of light was measured by:

$$I_o = 3.559 \times 10^{-6} x \text{ Einst/s} \quad (1)$$

$$x = x_2 - x_1 \quad (2)$$

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

Measurement of Acidity:

Hydrogen ion activity was determined in terms of Hammett acidity function ( $H_o$ ). An optical method was adopted using acridine as a basic indicator for the determination of the acidity of the reaction solution<sup>12</sup>.

$$H_o = -\log h_o \quad (3)$$

For basic indicator hydrogen ion activity is

$$H_o = pK + \log \frac{[B]}{[BH^+]} \quad (4)$$

If the extinction of the indicator in extreme acidic and basic solutions is ' $d_1$ ' and ' $d_2$ ' then for a solution of intermediate acidity the extinction ' $d$ ' could be represented as

$$\frac{[B]}{[BH^+]} = \frac{d_1 - d}{d - d_2} \quad (5)$$

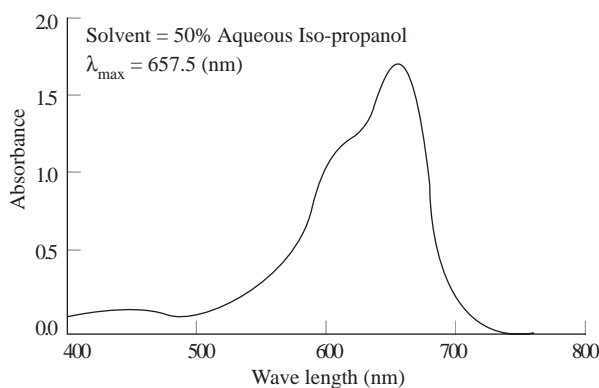
Acidity of solution ( $H_o$ ) was determined by the following relation:

$$H_o = pK + \log \frac{d_1 - d}{d - d_2} \quad (6)$$

The pK value for aqueous acridine solution<sup>12</sup> was taken as  $5.45 \pm 0.05$ . The acidity range was selected as 3.94 to 7.31.

## Results and Discussion

Dye solutions were prepared in the range  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  mol.dm<sup>-3</sup> in 50% (v/v) aqueous isopropanol. Wavelength maxima and a molar absorption coefficient of  $1.0 \times 10^{-6}$  mol.dm<sup>-3</sup> methylene green in 50% aqueous isopropanol were determined with a Shimadzu U V spectrophotometer. The value of  $\lambda_{\max}$  was found to be 657 nm and the molar absorptivity coefficient was found to be  $1.40 \times 10^5$  mol.dm<sup>-3</sup>.cm<sup>-1</sup> for  $1.0 \times 10^{-6}$  mol.dm<sup>-3</sup> methylene green solution in 50% aqueous isopropanol solvent. The representative spectra are shown in Figure 3. The rate of decay of methylene green was determined in terms of quantum yield ( $\varphi$ ), which is defined as moles of dye molecules of reactants converted into product per unit Einstein of light absorbed<sup>3</sup>:



**Figure 3.** Absorption spectra of methylene green in 50% aqueous isopropanol.

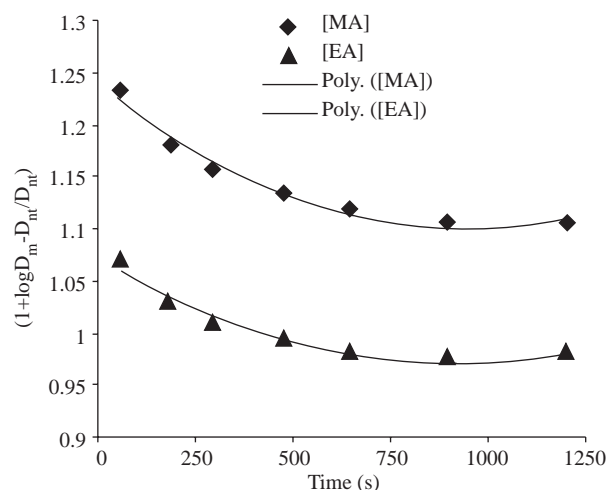
$$\varphi = \frac{\text{No. of moles of reactant } t \text{ converted into product}}{\text{No. of Einstein of light absorbed}} \quad (7)$$

The quantum yield ( $\varphi$ ) for the photochemical reduction of methylene green with reductants was calculated by the following relation<sup>12</sup>:

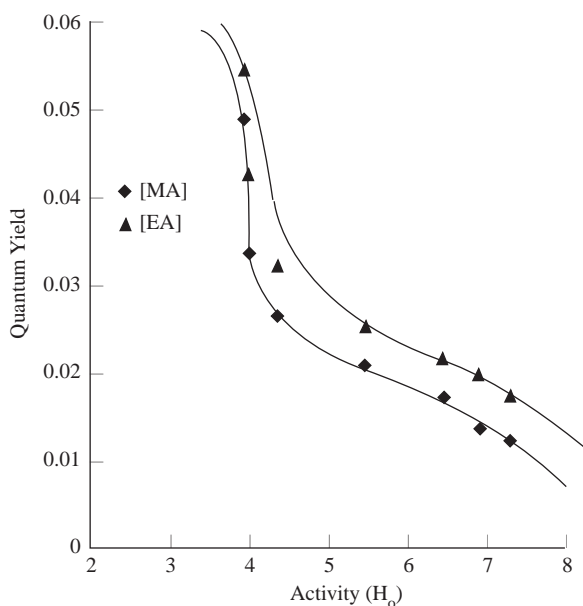
$$\frac{\epsilon \varphi L I_o (1 - \alpha)}{V} t = \log \left( \frac{D_m - D_{nt}}{D_{nt}} \right) - \log \left( \frac{D_m - D_{ni}}{D_{ni}} \right) \quad (8)$$

$$\log \left( \frac{D_m - D_{nt}}{D_{nt}} \right) = \frac{\epsilon \varphi L I_o (1 - \alpha)}{V} t + \log \left( \frac{D_m - D_{ni}}{D_{ni}} \right) \quad (9)$$

where  $D_{ni}$  is the deflection for the reaction mixture in the cell at initial conditions,  $\alpha$  is the fraction of light lost at each window,  $\epsilon$  is the molar absorptivity 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<sup>3</sup>,  $I_o$  is the initial intensity of the beam and  $(1 - \alpha)$  is the fraction of light transmitted through the window measured during the experiment. The plots of  $(D_m - D_{nt}) / D_{nt}$  versus time for the photochemical reduction of methylene green with methylamine and ethylamine at acidity ( $H_o$ ) = 4.00 are shown in Figure 4. Equation 6 is a straight line and the value of the slope was used to calculate the quantum yield. The quantum yield of the photochemical reduction of methylene green studied as a function of acidity<sup>19</sup>( $H_o$ ) is reported in Table 1. The results show that with the increase in the value of  $H_o$ , the quantum yield decreases for reductants, methylamine and ethylamine, and, at a fixed  $H_o$  value, a higher value of quantum yield was observed for ethylamine compared to methylamine. The plot for the effect of acidity on quantum yield is shown in Figure 5.



**Figure 4.** Plot of  $\log (D_m - D_{nt}) / D_{nt}$  versus time for photochemical reduction of methylene green with methylamine and ethylamine at  $H_o = 4.00$ .



**Figure 5.** Effect of acidities ( $H_o$ ) on quantum yield ( $\varphi$ ) for photochemical reduction of methylene green with methylamine and ethylamine concentration  $5.0 \times 10^{-2} \text{ mol.dm}^{-3}$ .

**Table 1.** Effect of acidity on quantum yield of photochemical reduction of methylene green with methylamine and ethylamine.

| Acidity<br>( $H_o$ ) | Quantum yield<br>( $10 \cdot \varphi$ )           |                   |
|----------------------|---|-------------------|
|                      | Methylamine                                       | Ethylamine        |
|                      | $[AH_2] = 5.0 \times 10^{-2} \text{ mol.dm}^{-3}$ |                   |
| 3.94                 | $0.488 \pm 0.002$                                 | $0.539 \pm 0.001$ |
| 4.00                 | $0.336 \pm 0.001$                                 | $0.427 \pm 0.003$ |
| 4.33                 | $0.300 \pm 0.003$                                 | $0.270 \pm 0.002$ |
| 5.44                 | $0.207 \pm 0.004$                                 | $0.251 \pm 0.001$ |
| 6.46                 | $0.198 \pm 0.002$                                 | $0.206 \pm 0.004$ |
| 6.90                 | $0.136 \pm 0.004$                                 | $0.196 \pm 0.004$ |
| 7.31                 | $0.122 \pm 0.003$                                 | $0.184 \pm 0.004$ |
|                      | $[AH_2] = 1.0 \times 10^{-2} \text{ mol.dm}^{-3}$ |                   |
| 3.94                 | $0.255 \pm 0.005$                                 | $0.398 \pm 0.002$ |
| 4.00                 | $0.187 \pm 0.003$                                 | $0.345 \pm 0.003$ |
| 4.33                 | $0.156 \pm 0.002$                                 | $0.256 \pm 0.004$ |
| 5.44                 | $0.139 \pm 0.001$                                 | $0.153 \pm 0.003$ |
| 6.46                 | $0.124 \pm 0.002$                                 | $0.125 \pm 0.003$ |
| 6.90                 | $0.103 \pm 0.002$                                 | $0.116 \pm 0.004$ |
| 7.31                 | $0.088 \pm 0.002$                                 | $0.108 \pm 0.002$ |

The effect of reactants on the quantum yield of photochemical reduction was studied in concentrations of reductants ranging from  $5.0 \times 10^{-2}$  to  $5.0 \times 10^{-1} \text{ mol. dm}^{-3}$ . The acidity of the reaction mixture was maintained using an acetate buffer system, as fixed volumes of dye solution, acid, base and buffer were taken. The results summarised in Table 2 show that the quantum yield was increased by higher concentrations of methylamine and ethylamine at certain  $H_o$  and dye concentrations. The high values of quantum yield for

ethylamine show that it is more reactive than methylamine. It was also observed that quantum yield was not affected much by the change in concentration of methylene green as shown in Table 3. This independence was also observed by Matsumoto<sup>5</sup> and Uddin<sup>12</sup>.

**Table 2.** Effect of concentration of reductants on quantum yield of photochemical reduction of methylene green.

| 10 . [AH <sub>2</sub> ]<br>(mol.dm <sup>-3</sup> ) | Quantum yield<br>(10 . φ) |               |
|--|---------------------------|---------------|
|  | Methylamine               | Ethylamine    |
| H <sub>o</sub> = 4.00                              |                           |               |
| 0.05   | 0.091 ± 0.001             | 0.141 ± 0.005 |
| 0.10   | 0.095 ± 0.005             | 0.158 ± 0.002 |
| 0.20   | 0.130 ± 0.001             | 0.166 ± 0.004 |
| 0.50   | 0.146 ± 0.002             | 0.219 ± 0.001 |
| 1.00   | 0.187 ± 0.003             | 0.345 ± 0.005 |
| 5.00   | 0.336 ± 0.002             | 0.428 ± 0.002 |
| H <sub>o</sub> = 7.31                              |                           |               |
| 0.05   | 0.027 ± 0.003             | 0.031 ± 0.004 |
| 0.10   | 0.039 ± 0.001             | 0.050 ± 0.001 |
| 0.20   | 0.062 ± 0.002             | 0.065 ± 0.001 |
| 0.50   | 0.075 ± 0.001             | 0.098 ± 0.002 |
| 1.00   | 0.088 ± 0.002             | 0.108 ± 0.002 |
| 5.00   | 0.122 ± 0.003             | 0.184 ± 0.004 |

**Table 3.** Effect of concentration of methylene green on quantum yield of photochemical reduction of methylene green with reductant

| 10 <sup>6</sup> . [MG]<br>(mol.dm <sup>-3</sup> ) | Quantum yield<br>(10 . φ) |               |
|---|---------------------------|---------------|
|   | Methylamine               | Ethylamine    |
| 0.2   | 0.092 ± 0.002             | 0.139 ± 0.001 |
| 0.4   | 0.092 ± 0.002             | 0.136 ± 0.002 |
| 0.8   | 0.090 ± 0.001             | 0.130 ± 0.002 |
| 1.2   | 0.087 ± 0.003             | 0.126 ± 0.001 |
| 1.6   | 0.086 ± 0.003             | 0.126 ± 0.001 |
| 2.0   | 0.085 ± 0.003             | 0.125 ± 0.002 |

The influence of temperature on quantum yield was studied at different H<sub>o</sub> values, from 293 to 313 K. The results in Table 4 show at a fixed value of H<sub>o</sub>, the values of quantum yield increase with increases in temperature and decrease with increases in H<sub>o</sub> values. Higher average temperature coefficients were observed for ethylamine compared to methylamine.

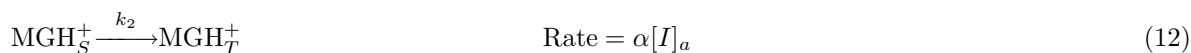
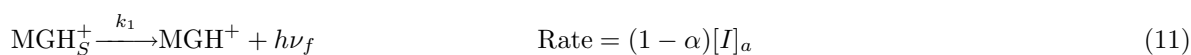
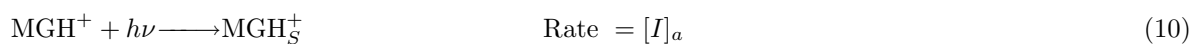
### The mechanism steps of the photochemical reduction of methylene green

On the basis of the above results, the mechanism of photochemical reduction may be proposed by the following steps on account of certain processes:



**Table 4.** Effect of temperature on quantum yield of photochemical reduction of methylene green with reductants.

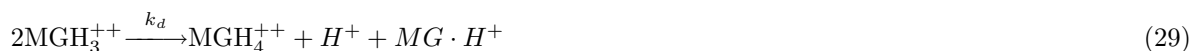
| Reductant          | Acidity (H <sub>o</sub> ) | Quantum yield (10 . φ)           |                                  |                                  |                                  |               |
|--------------------|---------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|---------------|
|                    |                           | Temperature (K)                  |                                  |                                  |                                  |               |
| [AH <sub>2</sub> ] |                           | 293                              | 298                              | 303                              | 308                              | 3130          |
| Methylamine        | 4.00                      | 0.147 ± 0.002                    | 0.162 ± 0.002                    | 0.190 ± 0.002                    | 0.199 ± 0.002                    | 0.213 ± 0.003 |
|                    | 7.31                      | 0.050 ± 0.002                    | 0.097 ± 0.002                    | 0.104 ± 0.002                    | 0.114 ± 0.003                    | 0.123 ± 0.003 |
| Ethylamine         | 4.00                      | 0.301 ± 0.001                    | 0.331 ± 0.001                    | 0.389 ± 0.001                    | 0.407 ± 0.003                    | 0.457 ± 0.003 |
|                    | 7.31                      | 0.134 ± 0.001                    | 0.199 ± 0.001                    | 0.218 ± 0.002                    | 0.301 ± 0.001                    | 0.346 ± 0.004 |
|                    |                           | Temperature coefficients         |                                  |                                  |                                  |               |
|                    |                           | φ <sub>25</sub> /φ <sub>20</sub> | φ <sub>30</sub> /φ <sub>25</sub> | φ <sub>35</sub> /φ <sub>30</sub> | φ <sub>40</sub> /φ <sub>35</sub> | Average       |
| Methylamine        | 4.00                      | 1.10                             | 1.17                             | 1.04                             | 1.07                             | 1.07 ± 0.05   |
|                    | 7.31                      | 1.94                             | 1.07                             | 1.09                             | 1.07                             | 1.29 ± 0.1    |
| Ethylamine         | 4.00                      | 1.09                             | 1.17                             | 1.04                             | 1.12                             | 1.11 ± 0.05   |
|                    | 7.31                      | 1.48                             | 1.09                             | 1.38                             | 1.14                             | 1.27 ± 0.20   |



$$K_1 = \frac{k_7}{k_8} = \frac{[\text{MGH}_{2T}^{++}]}{[\text{MGH}_T^+][\text{H}^+]}$$



$$K_2 = \frac{k_{13}}{k_{14}} = \frac{[\text{MGH}_{2T}^{++} \cdot \text{AH}_2]}{[\text{MGH}_{2T}^{++}] [\text{AH}_2]}$$



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

$$\begin{aligned} \alpha [I]_a = & [k_5 [\text{MGH}_T^+] [\text{AH}_2] + k_6 [\text{MGH}_T^+] + k_9 [\text{MGH}_T^+] [\text{AH}_2] + \\ & k_{10} [\text{MGH}_{2T}^{++}] [\text{AH}_2] + k_{11} [\text{MGH}_{2T}^{++}] [\text{AH}_2] + \\ & k_{12} [\text{MGH}_{2T}^{++}] + k_{15} [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] + k_{16} [\text{MGH}_{2T}^{++}] + \\ & k_{17} [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] [\text{MGH}^+] + k_{18} [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] [\text{MGH}^+] ] \end{aligned} \quad (31)$$

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.

$$\text{Rate of disappearance of methylene green} = -\frac{d[\text{MGH}^+]}{dt}$$

$$\begin{aligned} -\frac{d[\text{MGH}^+]}{dt} = & \frac{1}{2} [k_9 [\text{MGH}_T^+] [\text{AH}_2] + k_{10} [\text{MGH}_{2T}^{++}] [\text{AH}_2] + \\ & k_{16} [\text{MGH}_{2T}^{++}] + k_{17} [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] [\text{MGH}^+] + \\ & k_{18} [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] [\text{MGH}^+] ] \end{aligned} \quad (32)$$

Let

$$[\text{MGH}_T^+] = a, [\text{MGH}_{2T}^{++}] = b, [\text{MGH}_{2T}^{++} \cdot \text{AH}_2] = c, [\text{MGH}^+] = d,$$

$$[\text{AH}_2] = \ell \text{ and } [H^+] = h_o$$

Substituting these symbols in equations 31 and 32:

$$\alpha[I]_a = [k_5al + k_6a + k_9al + k_{10}bl + k_{11}bl + k_{12}b + k_{15}c + k_{16}b + k_{17}cd + k_{18}cd] \quad (33)$$

$$-\frac{d[\text{MGH}^+]}{dt} = \frac{1}{2} [k_9al + k_{10}bl + k_{16}b + k_{17}cd + k_{18}cd] \quad (34)$$

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 33 and 34:

$$\alpha[I]_a = [k_5al + k_6a + k_9al + k_{10}bl + k_{11}bl + k_{12}b + k_{15}c + k_{16}b + kr_{17}cd] \quad (35)$$

$$-\frac{d[\text{MGH}^+]}{dt} = \frac{1}{2} [k_9al + k_{10}bl + k_{16}b + k_{17}cd] \quad (36)$$

The quantum yield ( $\varphi$ ) of the photochemical reaction is defined as

$$\varphi = \frac{-d[\text{MGH}^+]/dt}{[I]_a} \quad (37)$$

Substituting equations 35 and 36 in equation 37:

$$\varphi = \frac{\alpha}{2} \frac{[k_9al + k_{10}bl + k_{16}b + k_{17}cd]}{\left[ \begin{array}{l} k_5al + k_6a + k_9al + k_{10}bl + k_{11}bl + \\ k_{12}b + k_{15}c + k_{16}b + k_{17}cd \end{array} \right]} \quad (38)$$

According to mechanism steps 11 and 16:

$$K_1 = \frac{b}{ah_o} \quad (39)$$

$$b = \mathbf{K}_1ah_o \quad (40)$$

$$K_2 = \frac{c}{bl} \quad (41)$$

$$c = \mathbf{K}_2bl \quad (42)$$

Put the value of b:

$$c = \mathbf{K}_2 \mathbf{K}_1ah_o\ell \quad (43)$$

Substituting the values of 'b' and 'c' from equations 40 and 41 in equation 38:

$$\varphi = \frac{\alpha}{2} \frac{[k_9al + \mathbf{K}_1h_o[(k_{10}\ell + k_{16}) + \mathbf{K}_2k_{17}ld]]}{\left[ \begin{array}{l} k_5\ell + k_6 + k_9\ell + \mathbf{K}_1h_o + \left[ \begin{array}{l} k_{10}\ell + k_{11}\ell + k_{12} + k_{16} \\ +\mathbf{K}_2k_{15}\ell + \mathbf{K}_2k_{17}ld \end{array} \right] \end{array} \right]} \quad (44)$$

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

At high acidity, the species  $[\text{MGH}_7^+]$  is not supposed to be present; therefore the

mechanism steps involving  $[\text{MGH}_T^+]$  have been neglected and equation 35 is reduced to

$$\varphi_1 = \frac{\alpha}{2} \frac{[\mathbf{K}_1 h_o (k_{10}\ell + k_{16} + \mathbf{K}_2 k_{17}\ell d)]}{\mathbf{K}_1 h_o (k_{10}\ell + k_{11}\ell + k_{12} + k_{16} + \mathbf{K}_2 k_{15}\ell + \mathbf{K}_2 k_{17}\ell d)} \quad (45)$$

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

$$\varphi_{1(\text{Solvent})} = \frac{\alpha}{2} \frac{(k_{12} + k_{16})}{k_{16}} \quad (46)$$

At low  $h_o$ ,  $\varphi = \varphi_2$  and  $[\text{MGH}_{2T}^{++}]$ ,  $[\text{MGH}_{2T}^{++} \cdot \text{AH}_2]$  are not supposed to be present; thus equation 44 reduces to

$$\varphi_2 = \frac{\alpha}{2} \frac{k_9\ell}{k_5\ell + k_6 + k_9\ell} \quad (47)$$

where  $\varphi_2$  is the quantum yield at low acidity.

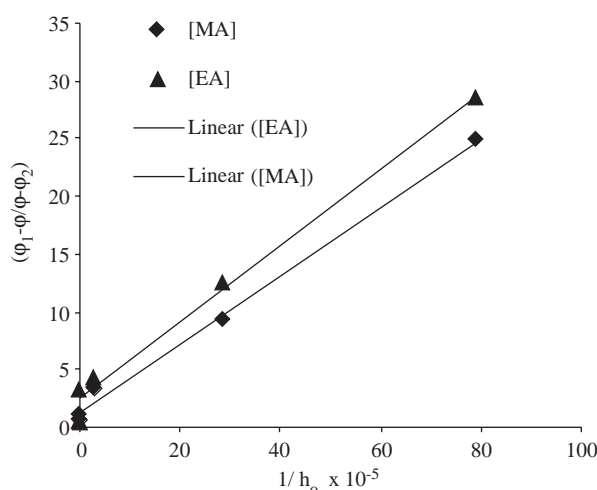
$$\frac{\varphi_1 - \varphi}{\varphi - \varphi_2} = \frac{\varphi_1}{\varphi_2} \frac{k_9\ell}{\mathbf{K}_1 h_o (k_{10}\ell + k_{16} + \mathbf{K}_2 k_{17}\ell d)} \quad (48)$$

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

$$\frac{\varphi_1 - \varphi}{\varphi - \varphi_2} = \frac{\varphi_1}{\varphi_2} \frac{k_9}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17}d)} \cdot \frac{1}{h_o} \quad (49)$$

Equation 49 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 6.



**Figure 6.** Plot of  $(\varphi_1 - \varphi) / (\varphi - \varphi_2)$  versus  $1/h_o$  for photochemical reduction of methylene green with methylamine and ethylamine at concentration  $5.0 \times 10^{-2} \text{ mol.dm}^{-3}$ .

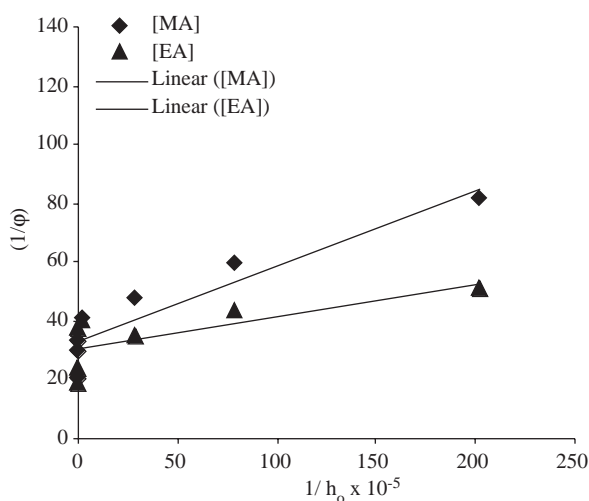
The complexity of the ratios of rate constants can be removed by fixing some limitations and by neglecting less contributing rate constants, the simple ratios for expected rate constants can be obtained. Again referring to equation 45, and neglecting  $k_6$ ,  $k_9$  and  $k_{16}$ :

$$\frac{1}{\varphi} = \frac{2}{\alpha} \frac{k_{10}\ell + k_{11}\ell + k_{12} + \mathbf{K}_2 k_{15}\ell + \mathbf{K}_2 k_{17}ld}{k_{10}\ell + \mathbf{K}_2 k_{17}ld} + \frac{2}{\alpha} \frac{k_5}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17}d)} \cdot \frac{1}{h_o} \quad (50)$$

Equation 50 shows the relationship between  $1/\varphi$  and  $1/h_o$ , representing a straight line plot with slope  $\frac{2}{\alpha} \frac{k_5}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17}d)}$

and intercept  $\frac{2}{\alpha} \frac{k_{10}\ell + k_{11}\ell + k_{12} + \mathbf{K}_2 k_{15}\ell + \mathbf{K}_2 k_{17}ld}{k_{10}\ell + \mathbf{K}_2 k_{17}ld}$ .

A representative plot showing the effect of  $1/\varphi$  versus  $1/h_o$  is shown in Figure 7.



**Figure 7.** Plot of reciprocal of quantum yield ( $1/\varphi$ ) versus  $1/h_o$  for photochemical reduction of methylene green with methylamine and ethylamine at concentration  $5.0 \times 10^{-2} \text{ mol.dm}^{-3}$ .

At a constant concentration of reactant  $k_5$  can be neglected as  $[\text{MGH}_T^+]$  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:

$$\frac{1}{\varphi} = \frac{2}{\alpha} \frac{\mathbf{K}_2 k_{17}d}{k_{10} + \mathbf{K}_2 k_{17}d} + \frac{2}{\alpha} \frac{k_6}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17}d)} \cdot \frac{1}{h_o} \quad (51)$$

Equation 51 shows the relationship between  $\frac{1}{\varphi}$  and  $\frac{1}{h_o}$ , representing a straight line plot with slope  $\frac{2}{\alpha} \frac{k_6}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17}d)}$  and intercept  $\frac{2}{\alpha} \frac{\mathbf{K}_2 k_{17}d}{k_{10} + \mathbf{K}_2 k_{17}d}$ .

The relation between quantum yield and reductant concentration is given by

$$\frac{1}{\varphi} = \frac{2}{\alpha} + \frac{2}{\alpha} \frac{k_{11} + \mathbf{K}_2 k_{15}}{k_{10} + \mathbf{K}_2 k_{17}d} + \frac{2}{\alpha} \frac{k_{12}}{k_{10} + \mathbf{K}_2 k_{17}d} \cdot \frac{1}{\ell} \quad (52)$$

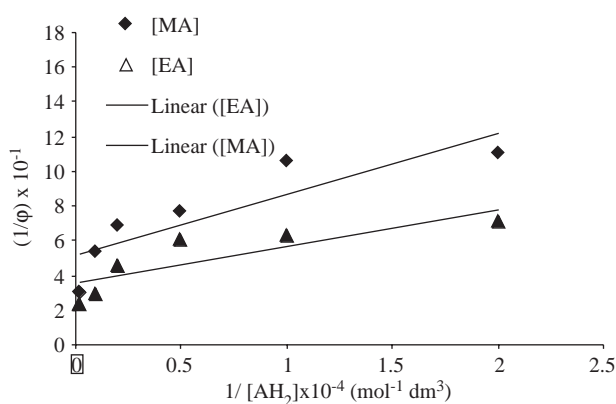
This equation, 52, shows the direct relation between  $1/\varphi$  and  $1/\ell$ , i.e.  $1/[AH_2]$ . The plot is a straight line having a slope and intercept as follows:

$$\text{Slope} = \frac{2}{\alpha} \frac{k_{12}}{k_{10} + K_2 k_{17} d}, \text{Intercept} = \frac{2}{\alpha} + \frac{2}{\alpha} \frac{k_{11} + K_2 k_{15}}{k_{10} + K_2 k_{17} d}$$

The intercept shows the quantum yield at infinite concentration and so equation 52 can be written as

$$\frac{1}{\varphi} = \frac{1}{\varphi_\alpha} + \frac{2}{\alpha} \frac{k_{12}}{k_{10} + K_2 k_{17} d} \cdot \frac{1}{\ell} \quad (53)$$

A representative plot showing the effect of reductant concentration on quantum yield as  $1/\varphi$  versus  $1/[AH_2]$  is shown in Figure 8.



**Figure 8.** Plot of reciprocal of quantum yield ( $1/\varphi$ ) versus  $1/[AH_2]$  for photochemical reduction of methylene green with methylamine and ethylamine at  $H_0 = 4.00$ .

The values of ratios of certain rate constants obtained by the proposed mechanism for photochemical reduction are tabulated in Table 5. 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:



and the second when protonated triplet excited state is associated with a reductant molecule establishing an equilibrium state.



The representative Figure 5 also represents the 2 equilibria, the first at high acidity and the second for the association of the protonated triplet excited state with reductant. Results for equilibrium constants, reported in Table 6, show that the values of  $K_1$  and  $K_2$  obtained were  $3.67 \times 10^{-6}$  and  $5.07 \times 10^{14} \text{ mol}^{-1} \cdot \text{dm}^3$  respectively, which were also supported by the results of dependence of quantum yield ( $\varphi$ ) on acidity  $H_0$ .

The values of equilibrium constants are also comparable with reported values for  $\mathbf{K}_1^{1,13}$  of  $10^{-6} \text{ mol}^{-1} \cdot \text{dm}^3$  and for  $\mathbf{K}_2^{1,14}$  of  $1.0 \times 10^{14} \text{ mol}^{-1} \cdot \text{dm}^3$ .

**Table 5.** Ratios of rate constants of the proposed mechanism of photochemical reduction of methylene green with reductants.

| Ratios of rate constants  | Reductant     |               |
|---|---------------|---------------|
|   | Methylamine   | Ethylamine    |
| $\frac{2}{\alpha} \frac{k_5 + k_9}{k_9}$  | 95.984 ± 3    | 73.515 ± 2    |
| $\frac{2}{\alpha} \frac{k_6}{k_9} \cdot 10^3$   | 14.165 ± 0.03 | 12.678 ± 0.02 |
| $\frac{2}{\alpha} \frac{k_{12}}{k_{10} + \mathbf{K}_2 k_{17} d} \cdot 10^3$   | 3.507 ± 0.10  | 2.145 ± 0.31  |
| $\frac{2}{\alpha} \frac{k_{10} + k_{11} + k_{15} \mathbf{K}_2 + \mathbf{K}_2 k_{17} d}{k_{10} + \mathbf{K}_2 k_{17} d}$ | 51.636 ± 9    | 35.081 ± 29   |
| $\frac{2}{\alpha} \frac{k_5}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17} d)} \cdot 10^6$                                 | 27.773 ± 0.7  | 1.274 ± 0.5   |
| $\frac{2}{\alpha} \frac{k_6}{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17} d)} \cdot 10^6$                                 | 2.912 ± 0.7   | 2.753 ± 1.1   |
| $\frac{2}{\alpha} \frac{\mathbf{K}_2 k_{17} d}{k_{10} + \mathbf{K}_2 k_{17} d}$   | 61.157 ± 6    | 47.280 ± 9    |
| $\frac{\mathbf{K}_1 (k_{10} + \mathbf{K}_2 k_{17} d)}{k_9} \cdot 10^6$  |               |               |
| (i) at low [AH <sub>2</sub> ]   | 1.227 ± 0.3   | 4.595 ± 0.9   |
| (ii) at high [AH <sub>2</sub> ]   | 2.944 ± 0.3   | 3.799 ± 0.9   |
| $\frac{k_5}{\mathbf{K}_1 k_{16}} \cdot 10^3$  | 8.304 ± 0.05  | 1.283 ± 0.02  |
| $\frac{k_6}{k_5 k_9} \cdot 10^4$  | 1.475 ± 0.03  | 1.724 ± 0.3   |
| $\frac{k_{16}}{k_{10} + k_{11} + k_{15} \mathbf{K}_2 + \mathbf{K}_2 k_{17} d} \cdot 10^5$                               | 6.791 ± 0.3   | 6.116 ± 0.5   |

**Table 6.** Specific rate constants of mechanism of photochemical reduction of methylene green with reductants.

| Specific rate Constant   | Reductant             |                       |
|--|-----------------------|-----------------------|
|  | Methylamine           | Ethylamine            |
| $k_5 \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$    | $2.78 \times 10^5$    | $1.27 \times 10^4$    |
| $k_9 \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$    | $2.94 \times 10^5$    | $3.79 \times 10^5$    |
| $k_{11} \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$ | $3.96 \times 10^{17}$ | $2.57 \times 10^{17}$ |
| $k_{12} \text{ (s}^{-1}\text{)}$                               | $3.37 \times 10^{13}$ | $2.15 \times 10^{13}$ |
| $k_{15} \text{ (s}^{-1}\text{)}$                               | $8.22 \times 10^3$    | $6.41 \times 10^3$    |
| Equilibrium constant   | Experimental          | Literature            |
| $\mathbf{K}_1 \text{ (mol}^{-1} \text{ dm}^3 \text{)}$         | $3.67 \times 10^{-6}$ | $10^{-6}$             |
| $\mathbf{K}_2 \text{ (mol}^{-1} \text{ dm}^3 \text{)}$         | $5.07 \times 10^{14}$ | $1.0 \times 10^{14}$  |

The temperature dependence of experimental rate was used to study the thermodynamics of the reaction in terms of activation parameters. Results for activation parameters are reported in Table 7. This shows that thermodynamic parameters are affected by the concentration of reductants and acidity of solutions. At high acidity ( $H_o$ ) values, higher values of activation parameters are obtained. The effect of temperature on quantum yield can be represented by the relation<sup>3,15</sup>

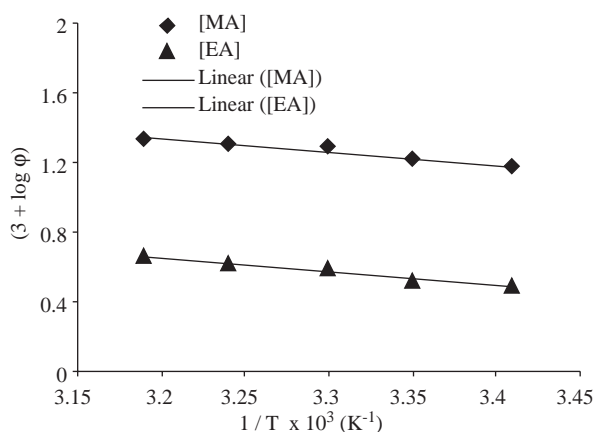
$$\varphi = A. \exp(-E_a/RT) \tag{54}$$

where A is the pre-exponential factor or frequency factor,  $E_a$  is the activation energy, T is the absolute temperature in K, and R is the gas constant. The slope of the linear plot of quantum yield ( $\log \varphi$ ) versus  $1/T$  gives the value of activation energy ( $E_a$ ) for the photochemical reduction process. The representative plot of quantum yield ( $\log \varphi$ ) versus  $1/T$  is shown in Figure 9. Some other thermodynamic quantities related to the reactants and the activated complex were drawn. In terms of the transition state theory the rate of a photochemical reaction may be considered to be determined from the enthalpy change, entropy change and free energy change of activation involved in the formation of activated complex and can be expressed as<sup>15,16</sup>

$$\Delta H^* = E_a - RT \quad (55)$$

**Table 7.** Thermodynamic parameters for photochemical reduction of methylene green with reductants at 298 K and at different acidities ( $H_o$ ).

| Thermodynamic Parameters   | Reductant       |                 |                 |                 |
|--|-----------------|-----------------|-----------------|-----------------|
|  | Methylamine     |                 | Ethylamine      |                 |
| ( $H_o$ )  | 4.00            | 7.31            | 4.00            | 7.31            |
| Energy of activation ( $E_a$ ) (kJ mol <sup>-1</sup> )   | 14.239 ± 1.8    | 29.896 ± 3.0    | 15.605 ± 1.4    | 32.854 ± 2.0    |
| Change in enthalpy of activation ( $\Delta H^\ddagger$ ) (kJ mol <sup>-1</sup> )               | 11.762 ± 0.05   | 27.418 ± 0.06   | 13.128 ± 0.07   | 30.377 ± 0.07   |
| Change in free energy of activation ( $\Delta G^\ddagger$ ) (kJ mol <sup>-1</sup> )            | 88.777 ± 0.9    | 118.183 ± 1.2   | 93.290 ± 2.1    | 126.295 ± 2.4   |
| Change in entropy of activation ( $\Delta S^\ddagger$ ) (J.K <sup>-1</sup> mol <sup>-1</sup> ) | - 258.441 ± 0.2 | - 304.582 ± 0.1 | - 268.999 ± 0.2 | - 321.874 ± 0.2 |



**Figure 9.** Plot of  $\log \varphi$  versus  $1/T$  for photochemical reduction of methylene green with methylamine and ethylamine at  $H_o = 4.00$ .



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

$$A = \frac{KT}{h} \exp(\Delta S^*/R) \quad (56)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (57)$$

where  $\Delta G^*$  is the free energy change of activation,  $\Delta H^*$  is the enthalpy change of activation,  $\Delta S^*$  is the entropy change of activation, K is Boltzmann's constant and h is Planck's constant.

The results for activation parameters in Table 7 show that the values of energy of activation ( $E_a$ ), enthalpy change of activation ( $\Delta H^*$ ) and free energy change of activation ( $\Delta G^*$ ) are higher for reduction due to ethylamine compared to methylamine. It is concluded that the formation of activated complex needs more energy for ethylamine. This behaviour may be due to the increase in the size of the alkyl group present in ethylamine rather in methylamine. The more negative value of the entropy change of activation ( $\Delta S^*$ ) led to the conclusion that the formation of activated complex is more favoured in the presence of ethylamine.

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