

# PHOTOCHEMICAL REDUCTION OF THIONINE WITH DIMETHYLAMINE

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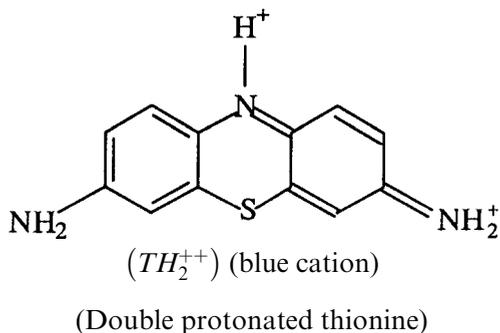
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## ABSTRACT

The photochemical reduction of thionine with dimethylamine was studied in 50% aqueous methanol at  $25 \pm 0.1^\circ\text{C}$  in a specially designed apparatus. The acidities of the solutions were determined using acetate buffers by a spectrophotometric method. The quantum yield ( $\phi$ ) of the photochemical reactions was determined at different concentrations of thionine and dimethylamine. It was found that the quantum yield is a function of the acidity as well as the concentration of reductant [ $AH_2$ ]. The results have been interpreted in terms of reaction mechanism. It was found that the quantum yield of the reactions of thionine with dimethylamine is controlled by two equilibria between (i) triplet state of thionine ( $^3TH^+$ ) with proton and protonated triplet state of thionine [ $^3T.H_2^{++}$ ] and (ii) protonated triplet state of thionine with reductant and associated complex of thionine with reductant [ $^3T.H_2^{++}.AH_2$ ].

## INTRODUCTION

Thionine in its singly protonated form  $TH^+$  is purple and exists as a monochloride in the pH range of 2-10. The doubly protonated cation  $TH_2^{++}$  is blue and appears in  $2.5 \text{ mol.dm}^{-3}$  hydrochloric acid or sulphuric acid.



On photoreduction, thionine is reduced partly or completely, depending upon the power of the reductant and the pH of the medium.

The photoreduction of thiazine dyes was studied by several researchers such as Kayser & Young (1976), Bonneau *et al.* (1974), Bonneau & Pereyre (1975) Guler Michael (1973) Guler & Aytakin, (1984), Solar *et al.* (1982) and Vonnach & Getoff (1983). Kayser & Young (1976) reported the complete photoreduction of thiazine dye and proposed the following mechanism:  $MBH^{\circ} \longrightarrow MBH \longrightarrow MBH_2$ .

Rate constants for the formation and decay of methylene blue semiquinone, atom-adduct on ring carbon and R-species in the pH range 1-4 was given by solar *et al.* (1982). Solar *et al.* (1982) also reported the values of dissociation constants. Bonneau *et al.* (1974), and Bonneau & Pereyre (1975) observed that triplet thionine is much better oxidant than methylene blue. Bonneau *et al.* (1974) discussed the large variation in quenching rate constant with the nature of the dye and the degree of protonation of the triplet state. They observed that the rate of photooxidation is very sensitive to pH changes from 5-9. Guler & Micheal (1973) studied photoreduction of methylene blue by water in acidic solution electrochemically. Vonnach & Getoff (1983) determined the rates of photobleaching and quantum yield using monochromatic light of wavelength 665 nm. The experiments were carried out in an inert condition using helium. The photochemical properties of thionine covalently bound to other macromolecules were studied by Viswanathan & Natarajan (1995a, b) and Sommer & Kramer (1971), Kramer & Maute (1973) reported that photooxygenation of allylthiourea with thionine as sensitizer takes place via radicals at high allylthiourea concentration. No further attention was devoted to the kinetic studies of photochemical reactions of thionine in the presence of organic reductants such as amines.

In the present work, photokinetic reduction of thionine with dimethylamine as a mild reducing agent was studied in an atmosphere of nitrogen by a light beam of  $5780 \pm 10 \text{ \AA}$  obtained by sets of filter solutions. The present study covers the effects of reductant concentration, solution acidity, dye concentration and temperature on the quantum yield ( $\phi$ ) of the reactions of thionine.

## EXPERIMENTAL

An optical bench housed in a dark room was constructed as shown in Fig. 1. The photochemical reduction of thionine was performed in a double - walled temperature - controlled reaction cell as shown in Figure 2 having an oxygen free atmosphere inside due to flushing of nitrogen before the irradiation. Irradiation was carried out by parallel light beam of wave length  $5790 \text{ \AA}$  obtained by a Mazda lamp of mercury vapours. Intensity of light was measured by photocells ( $P_1$  and  $P_2$ ) and signals of photocells were noted through galvanometers ( $G_1$ ,  $G_2$ ) after a short time intervals, till the reduction of dye was

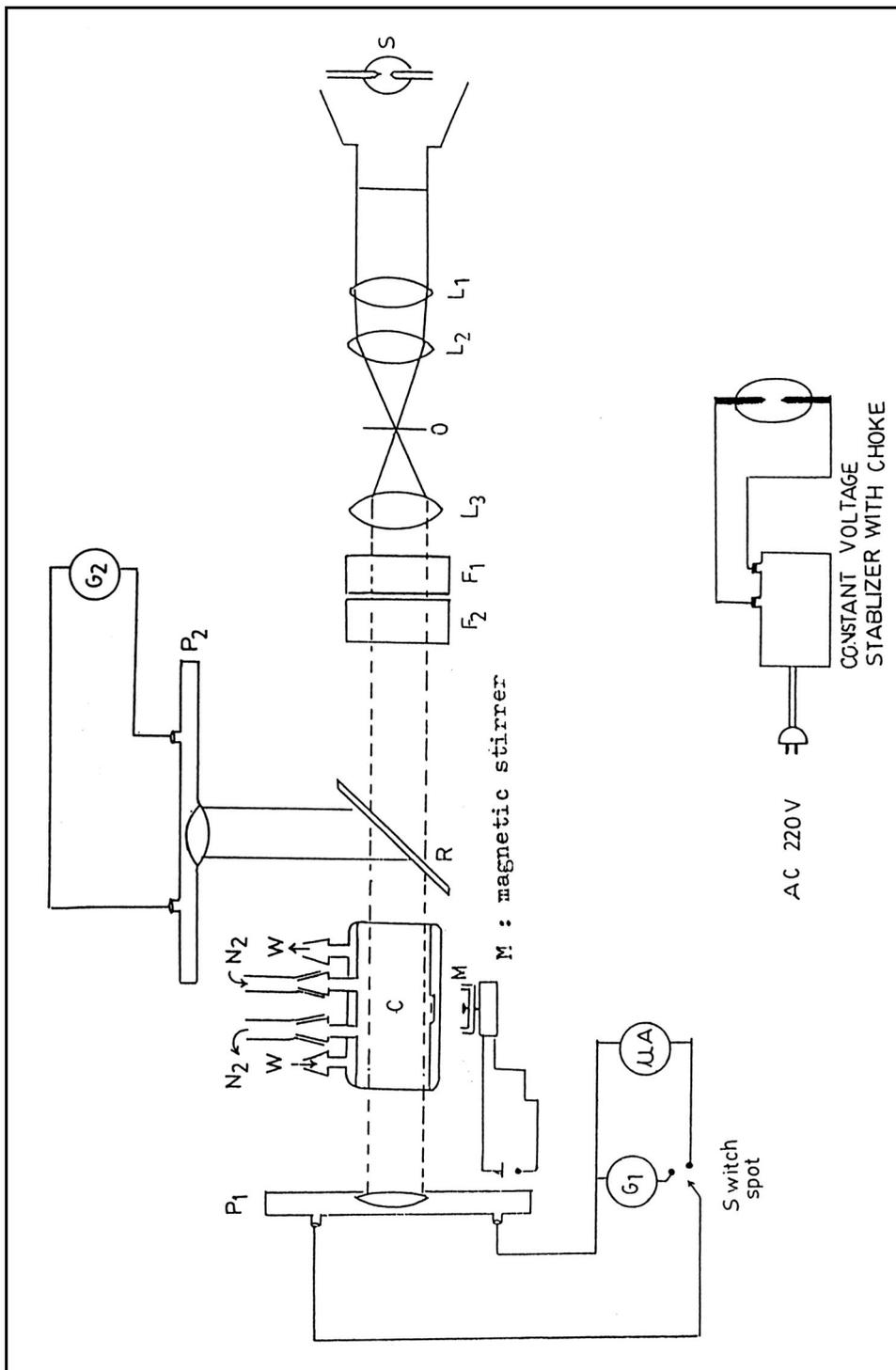


Figure 1: The optical bench.

completed and galvanometer showed a constant value. During the reaction, the temperature was controlled by flow of constant temperature water through the outer jacket of reaction cell. After the source, light was made to pass through convex lenses  $L_1$ ,  $L_2$  and  $L_3$ , and passed through a hole (o) of 2 mm diameter in between lenses  $L_2$  and  $L_3$ .

Monochromatic light of a narrow band of 5770Å to 5790Å was obtained by a set of filter solutions as suggested by Bowen (1942). R (a plain reflector) was used for reflection of a fraction of light to a reference photocell ( $P_2$ ), and the remaining fraction of light was passed through the reaction cell (C). This reaction cell is upgraded and modified as compared to the cell used by Atkins & (1958), Sawkar (1960) and Ahmed (1963).

Feiser's method (1924) was used to obtain dry - and oxygen - free nitrogen. In this method, 99.8% nitrogen was passed through a Dreschel bottle containing Feiser's solution.

Thionine indicator (Analar, E. Merck) was used. The molar extinction coefficient of thionine in 50% aqueous methanol was measured as  $4.70 \times 10^4 \text{ mol.}^{-1} \text{ dm.}^3 \text{ cm}^{-1}$  at 580 nm which is close to the value of  $4.90 \times 10^4 \text{ mol.}^{-1} \text{ dm.}^3 \text{ cm}^{-1}$  at 604 nm as calculated earlier (Fahimuddin 1996, 2000).

All the chemicals such as methanol, dimethylamine, sodium anthraquinone-2-sulphonate, lead acetate, sodium acetate, hydrochloric acid, sodium hydrosulphate, cupric chloride, calcium chloride, potassium dichromate, sulphuric acid and oxalic acid were of Analar grade from E. Merck. Extra pure quality of acridine orange with a  $\lambda_{\text{max}}$  of 489 nm was used. All stock solutions such as thionine, dimethylamine, sodium acetate, sodium hydroxide and sulphuric acid were prepared in 50% aqueous methanol. Stock solutions of thionine was preserved in well-stoppered polyethylene bottles as suggested by Sawkar (1960).

The mercury mazda lamp was turned on 30 minutes before the irradiation process began. Calculated volumes of thionine solution, reductant (dimethylamine) and buffer solution were pipetted into the reaction cell. The cell was then filled with the nitrogen retractable bubbler and outlet tap. The cell was magnetically stirred during the whole period of flushing and irradiation. After 40 minutes of flushing with nitrogen over the surface of solution was maintained during the irradiation process. Photocell responses were recorded with no cell in beam ( $D_o$ ), with the cell containing solvent ( $D_m$ ) and the cell containing reaction mixture ( $D_{nr}$ ). The transmission by the reaction mixture initially and after every 30 seconds was noted. The photocell responses corresponding to the incident light intensity with reaction cell out of the path of the beam was noted before and after the reaction.

### RESULTS AND DISCUSSION

Hydrogen ion activity is determined in terms of the Hammett acidity function,  $H_o$  as follows:

$$H_o = -\log h_o$$

whereas 
$$h_o = \frac{[H^+] f_{H^{+o}} f_B}{f_{BH^+}} \quad (1)$$

where  $f_B$ ,  $f_{BH}$  and  $f_{H^+}$  are the activity coefficients of a base indicator B, its protonated form  $BH^+$ , and the hydrogen ion  $[H^+]$  respectively. Sawkar (1960) used the  $pH$  method employing acid indicators such as bromophenol blue, thymol blue and bromocresol green for the determination of acidity of the reacting solution. In his opinion base indicators are suitable for the determination of acidity of solution, but he did not use base indicators. In this present work, an optical method (Fahimuddin *et al.* 1998, Fahimuddin 2000). was adopted, using acridine as a base indicator for the determination of the acidity of the reaction solution. The following formula was used:

$$H_o = pH - \log \frac{(d_1 - d)}{(d - d_2)} \quad (2)$$

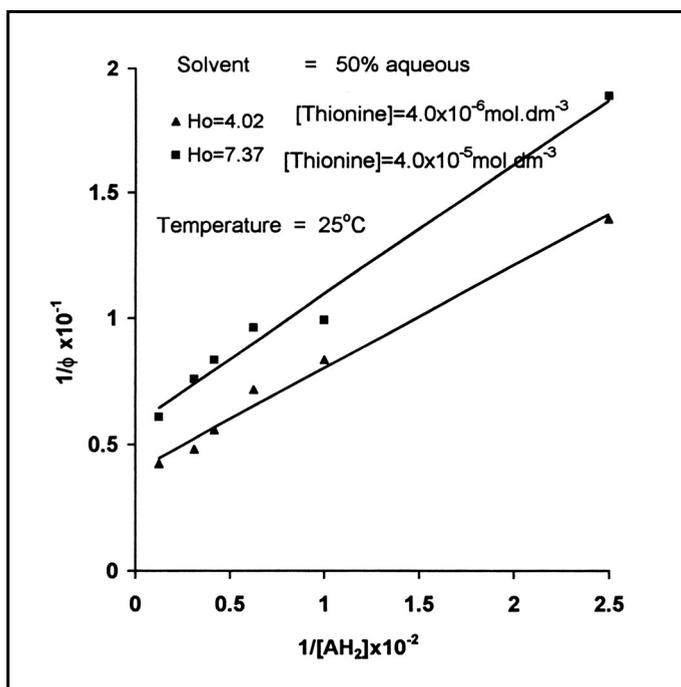


Figure 2: Plot of  $1/\phi$  against  $1/[AH_2]$ .

where  $d_1$  and  $d_2$  are the extinction of the indicator in extremely acidic and basic solutions respectively and  $d$  is the extinction of solutions of different acidities.

Quantum yield ( $\phi$ ) for the reaction of thionine with dimethylamine was calculated using the following expression:

$$\ln \left[ \frac{D_m - D_{nt}}{D_{ni}} \right] = - \frac{I_o \cdot (1 - \alpha) \cdot \epsilon \cdot \phi \cdot L \cdot t}{V} + \ln \frac{D_m - D_{ni}}{D_{ni}} \quad (3)$$

where  $D_m$ ,  $D_{ni}$  and  $D_{nt}$  stand for signals recorded for 50% aqueous methanol, reaction mixture in the cell at initial condition and reaction mixture in the cell at time  $t$  respectively.  $I_o$ , the light intensity;  $\alpha$ , the fraction of light lost at each window;  $\epsilon$ , the molar extinction coefficient for thionine in 50% aqueous methanol at 605 nm was taken as  $4.7 \times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ .  $L$ , the length of the path traveled by the beam in the cell was 6.0 cm.  $V$ , the volume of solution =  $0.0250 \text{ dm}^3$ .  $I_o$  and  $\alpha$  were determined during the course of experiments.

Equation (3) is a straight line equation with negative slope and intercept. The plot of  $\log \left[ \frac{D_m - D_{nt}}{D_{ni}} \right]$  against time 't' will be a straight line. The magnitude of slope is equal to  $I_o (1 - \alpha) \epsilon \phi L/V$ , from which quantum yield ( $\phi$ ) was calculated.

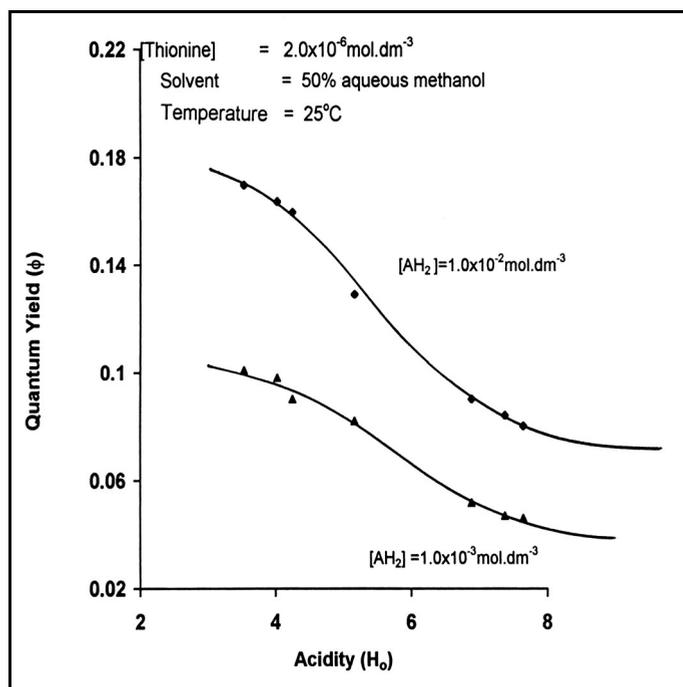


Figure 3: Plot of  $\phi$  versus  $H_0$ .

The effect of dimethylamine concentration on quantum yield was studied at two different acidities using 50% aqueous methanol as solvent. Results show that quantum yield is increased by increasing the concentration of reductant i.e. dimethylamine. The plots of reciprocal of quantum yield ( $1/\phi$ ) versus reciprocal of the concentration of dimethylamine  $1/[AH_2]$  are shown in Fig. 2. It was observed that the plots are straight lines with positive slopes. The values of quantum yield at infinite concentration of dimethylamine (DMA) were found to be 0.286 and 0.174 at acidities 4.02 and 7.37 respectively.

The influence of acidity on quantum yield was studied at two different concentrations of dimethylamine as  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-3} \text{ mol.dm}^{-3}$ . It was observed that quantum yield decreased with the increase in acidity. The  $H_o$  values were plotted against quantum yield as shown in Fig. 3. The reciprocal of quantum yield ( $1/\phi$ ) against the reciprocal of acidity ( $1/h_o$ ) was also plotted. The plots are straight lines with positive slopes as shown in Fig. 4. a & b The variation of  $(\phi_1 - \phi) / (\phi - \phi_2)$  with  $1/h_o$  was also studied. The plots of  $(\phi_1 - \phi) / (\phi - \phi_2)$  against  $1/h_o$  were drawn and shown in Figure 5. Here  $\phi_1$  and  $\phi_2$  are the extreme values of quantum yields at low and high acidities respectively. The above plots are straight lines passing through the origin.

Thionine (at various concentrations) and dimethylamine were irradiated in buffered methanol solutions while other parameters like temperature and acidity were kept constant in all sets of experiments. Results are tabulated in Table 1. The results show that quantum yield is independent of the concentration of thionine for fixed values of concentration of reductant and acidity. Matsumoto (1964) determined the values of quantum yields for the photoreduction of methylene blue in aqueous solutions with some derivatives of N-phenylglycine, and found that  $\phi$  is independent of light intensity and concentration of the dye. Fahimuddin (1996,

**Table 1.** Effect of Concentration of Thionine On  $\phi$  of Photochemical Reaction of Thionine

[Thionine] $\times 10^6$ mol.dm <sup>-3</sup>	$\phi$ with dimethylamine
1.0	0.091
2.0	0.091
2.5	0.090
3.0	0.091
3.5	0.091
$H_o$ : 4.02	Temperature : 25°
$[AH_2]$ : $1.6 \times 10^{-3} \text{ mol.dm}^{-3}$	Solvent : 50% aqueous methanol

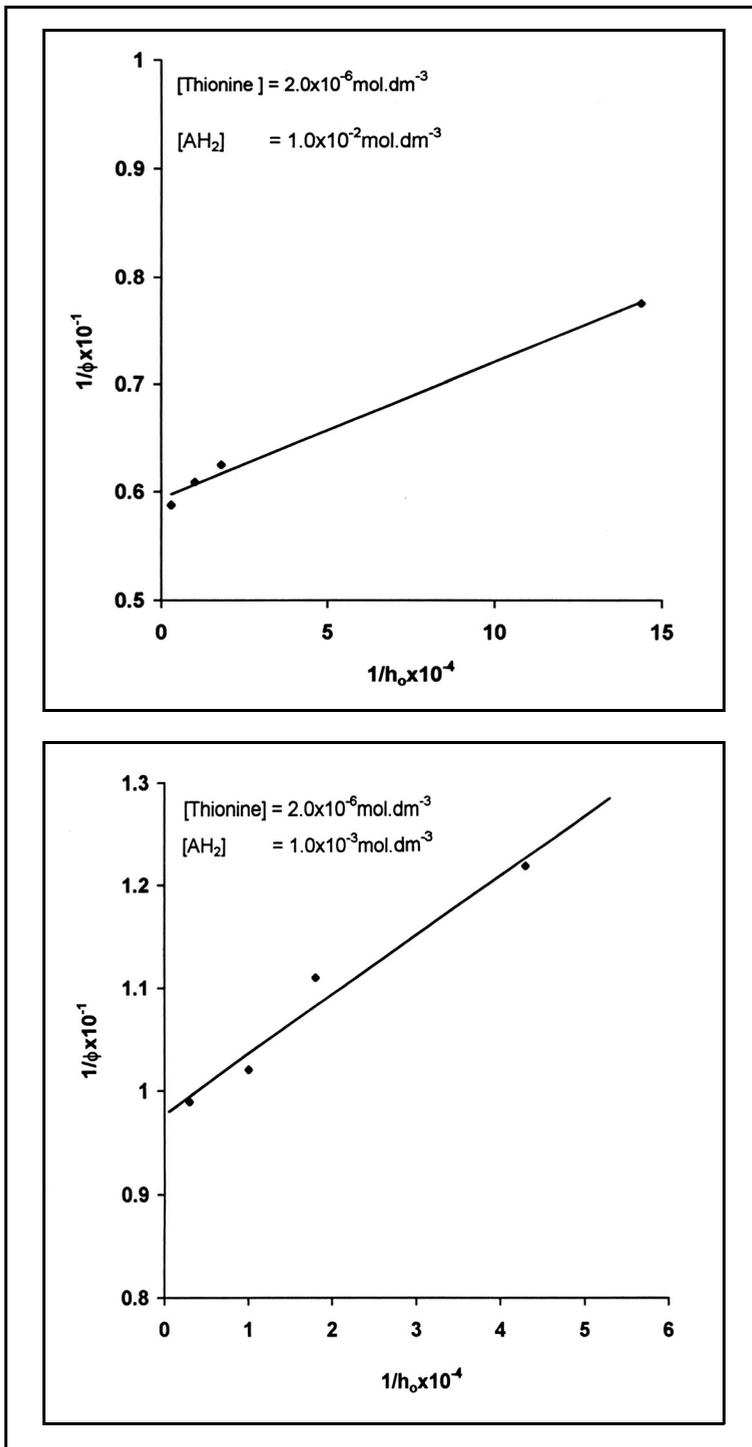


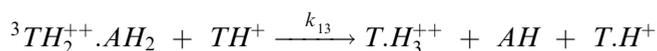
Figure 4: Plot of  $1/\phi$  versus  $1/h_0$ .

**Table 2.** Influence of Temperature on Quantum Yield of Photochemical Reaction of Thionine With Dimethylamine

	Temperature (°C)				
	15	20	25	30	35
$\phi$	0.115	0.131	0.151	0.173	0.198
Temperature coefficients	$\phi_{20}/\phi_{15}$	$\phi_{25}/\phi_{20}$	$\phi_{30}/\phi_{25}$	$\phi_{35}/\phi_{30}$	
	1.14	1.15	1.14	1.14	
[Thionine] :	$2.0 \times 10^{-6} \text{ mol.dm}^{-3}$		Temperature : 25°C		
[AH <sub>2</sub> ] :	$1.0 \times 10^{-2} \text{ mol.dm}^{-3}$		Solvent : 50% aqueous methanol		
H <sub>0</sub> :	4.02				

2000) also reported that quantum yield is independent of the concentration of thionine with N-phenylglycine and thiourea in absolute methanol.

The effect of temperature on quantum yield of the reactions of thionine was studied, and the results are summarized in Table 2. The data shows that as the temperature increases, quantum yield increases. It seems, therefore, that the reaction:



requires some activation energy.

The values of temperature coefficients for five different temperatures were calculated and tabulated in Table 2. The average value for temperature coefficient was found to be 1.14. These results are in agreement with those of Kostryokova & Dain (1955) and Fahimuddin (1996, 2000) reported earlier for thionine-glucose, thionine-N-phenylglycine and thionine-thiourea systems.

Experimental evidence led to the conclusion that the quantum yield of the reaction of thionine with dimethylamine in 50% aqueous methanol is a function of acidity. The plots between  $\phi$  and  $H_o$  as shown in Figure 3 are curved like a mirror image of the English letter 'S'. In these plots, sudden depression points are seen between the region of  $H_o = 4.25$  to  $H_o = 6.5$ . The point of inflection ( $H_o \sim 5$ , methanol/water) may be related to the protolytic equilibrium of the triplet state. Fischer (1964) determined the  $pK_T$  value as 6.3 in water which was redetermined by Faure *et al.* (1967) as 6.5 in water. This region looks like a transient region which controls the two precesses i.e. one is a product forming step and second should be the equilibrium between  ${}^3T.H_2^{++} \rightleftharpoons {}^3T.H^+ + H^+$ . The plots of  $1/\phi$  versus  $1/h_o$  and  $(\phi_1 - \phi) / (\phi - \phi_2)$  versus  $1/h_o$  as

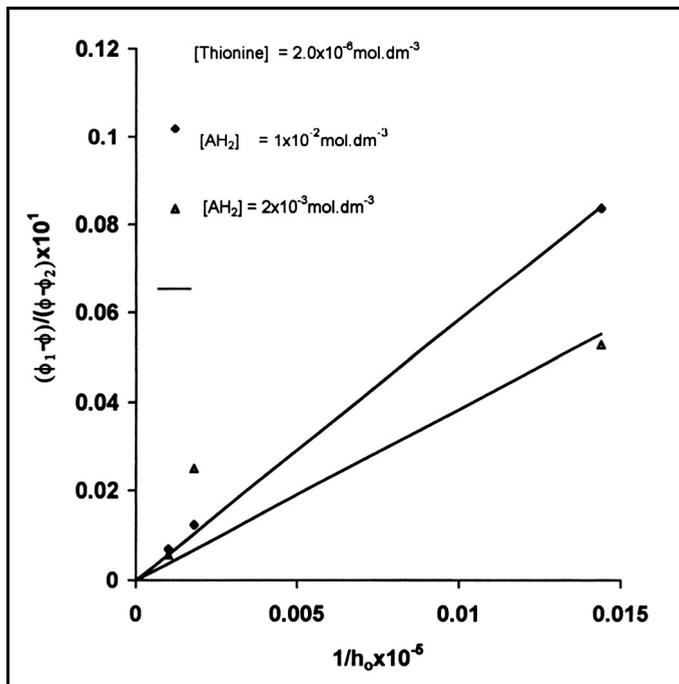
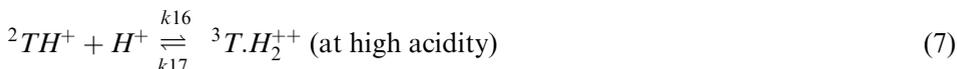
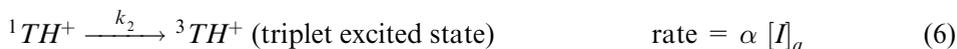
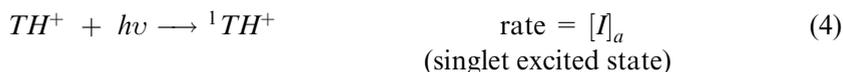


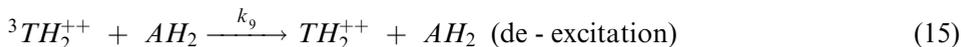
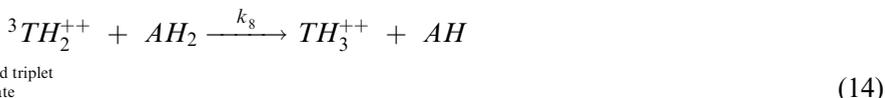
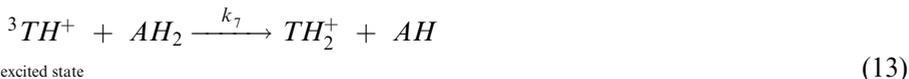
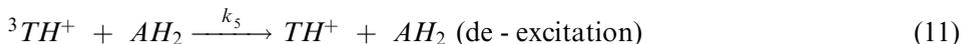
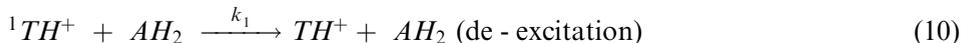
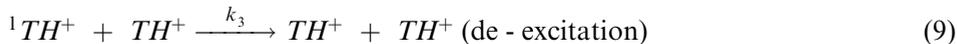
Figure 5: Plot of  $(\phi_1 - \phi) / (\phi - \phi_2)$  versus  $1/h_0$ .

drawn in Figs. 4 and 5 are straight lines with slopes that are a function of reductant concentration. No evidence of dependence of quantum yield on dye concentration was observed in the data, but the quantum yield was found to be influenced by varying concentrations of dimethylamine as illustrated in Fig. 2. Temperature dependency was also observed for this reaction.

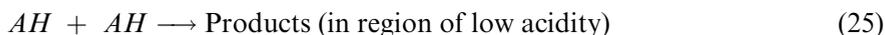
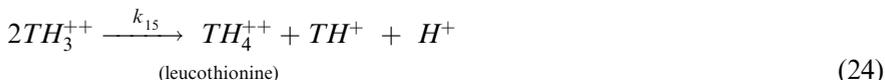
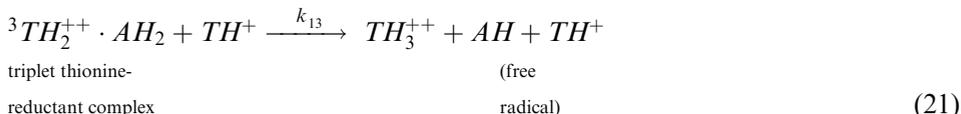
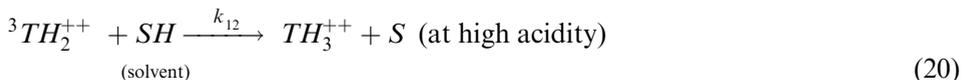
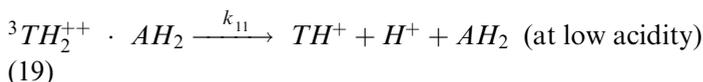
Based on the experimental evidence, a general mechanism for the photochemical reaction of thionine with dimethylamine is proposed consisting of the following steps.



$$\text{at equilibrium: } k_1 = \frac{k_{16}}{K_{17}} = \frac{[{}^3T.H_2^{++}]}{[{}^3TH^+][H^+]} = \frac{[{}^3T.H_2^{++}]}{[{}^3TH^+]} \cdot \frac{1}{h_0} \quad (8)$$



$$K_2 = \frac{k_{18}}{K_{19}} = \frac{[{}^3TH_2^{++} \cdot AH_2]}{[{}^3TH_2^{++}] [AH_2]} \quad (18)$$



In above steps,  $k_1$  to  $k_{21}$  represent the rate constants of each process.

**Derivation of rate equations:**

Let  $[I]_a$  be the quanta of light absorbed.  $[I]_a$  is calculated by adding the rate expressions of the suggested mechanism:

$$\begin{aligned} \alpha[I]_a = & k_5[{}^3TH^+][AH_2] + k_6[{}^3TH^+] + k_7[{}^3TH^+][AH_2] + \\ & k_8[{}^3TH_2^{++}][AH_2] + k_9[{}^3TH_2^{++}] + k_{10}[{}^3TH_2^{++}] + \\ & k_{11}[{}^3ThH_2^{++}][AH_2] + k_{12}[{}^3T.H_2^{++}] + k_{13}[{}^3ThH_2^{++} \cdot AH_2][TH^+]. \end{aligned} \quad (26)$$

The rate of disappearance of thionine is expressed as:

$$\begin{aligned} -\frac{d[TH^+]}{dt} = & \frac{1}{2} \left\{ k_7[TH_7^+][AH_2] + k_8[{}^3TH_2^{++}][AH_2] + k_{12}[{}^3TH_2^{++}] + \right. \\ & \left. K_{13}[{}^3TH_2^{++} \cdot AH_2][TH^+] + k_{14}[{}^3TH_2^{++} \cdot AH_2][TH^+] \right\}. \end{aligned} \quad (27)$$

Assuma that:

$$\begin{aligned} [TH_7^+] &= a, [TH_{2T}^{++}] = b, [{}^3TH_2^{++} \cdot AH_2] = c, \\ [TH^+] &= A, [AH_2] = l \text{ and } [H^+] = h_o. \end{aligned}$$

Substituting the symbols a, b, c, A, l and  $h_o$  in equations (26) and (27):

$$\alpha[I]_a = k_5al + k_6a + k_7al + k_8bl + k_9bl + k_{10}b + k_{11}c + k_{12}b + k_{13}cA \quad \text{and} \quad (28)$$

$$\frac{-d[Th.H^+]}{dt} = \frac{1}{2} \{ k_7al + k_8bl + k_{12}b + k_{22}cA \}$$

where  $k_{13} + k_{14} = k_{22}$

Quantum yield of the photochemical reaction is defined as:

$$\phi = \frac{-d[Th \cdot H^+]}{dt} / [I]_a, \quad (30)$$

$$\phi = \frac{\alpha}{2} \cdot \frac{k_7al + k_8bl + k_{12}b + k_{22}cA}{k_5al + k_6a + k_7al + k_8bl + k_9bl + k_{10}b + k_{11}c + k_{12}b + k_{13}cA} \quad (31)$$

Referring to equations (7) and (23), one gets:

$$b = K_1 a h_o, \quad c = K_2 b l \text{ or } c = K_1 K_2 a h_o l. \quad (32)$$

Substituting the values of b and c in equation (31):

$$\phi = \frac{\alpha}{2} \cdot \frac{k_7l + K_1 h_o (K_8l + k_{12}) + k_{22} \cdot K_1 K_2 \cdot h_o \cdot A l}{k_5l + k_6 + k_7l + K_1 h_o (k_8l + k_9l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 l A)} \quad (33)$$

At high acidity steps having  $[{}^3TH^+]$  have been neglected, therefore at high  $h_o$ ,  $\phi = \phi_1$  i.e.

$$\phi_1 = \frac{\alpha}{2} \cdot \frac{K_1 h_0 (k_8 l + k_{12} + k_{22} K_2 A l)}{K_1 h_0 (k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A)} \quad (34)$$

When  $l = 0$ , then

$$\phi_1 (\text{solvent}) = \frac{\alpha}{2} \cdot \frac{k_{12}}{(k_{10} + k_{12})} \quad (35)$$

At low  $h_0$ ,  $\phi = \phi_2$ .

At low acidity the species  $[^3TH_2^{++}]$  and  $[^3TH_2^{++} \cdot AH_2]$  are not present. Therefore steps involving these two species are eliminated. Then equation (31) reduces to:

$$\phi_2 = \frac{\alpha}{2} \cdot \frac{k_7 l}{(k_5 l + k_6 + k_7 l)} \quad (36)$$

From equation 33, 34 and 36, the relationship between  $(\phi_1 - \phi)/(\phi - \phi_2)$  and  $h_0$  is established as follows:

$$\frac{(\phi_1 - \phi)}{(\phi - \phi_2)} = \frac{k_5 l + k_7 l + k_6}{K_1 h_0 (k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 l A)} \quad (37)$$

The plot of  $(\phi_1 - \phi)/(\phi - \phi_2)$  against  $\frac{1}{h_0}$  is a straight line passing through the origin.

Again considering equation (34):

$$\frac{\alpha}{2} \cdot \frac{1}{\phi_1} = \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A}{k_8 l + k_{12} + k_{22} K_2 l A} + \frac{k_{12}}{k_8 l + k_{12} + k_{22} K_2 l A} \quad (38)$$

On neglecting  $k_{13}$  from the denominator:

$$\frac{1}{\phi_1} \cdot \frac{\alpha}{2} = \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A}{k_8 l + k_{22} K_2 l A} + \frac{k_{12}}{k_8 + k_{22} K_2 A} \cdot \frac{1}{l} \quad (39)$$

This expression is also a form of the equation of a straight line having both slope and intercept.

Again considering equation (36):

$$\frac{\alpha}{2} \cdot \frac{1}{\phi_2} = \frac{(k_5 l + k_7 l + k_6)}{k_7 l} = \frac{(k_5 + k_7)}{k_7} + \frac{k_6}{k_7} \cdot \frac{1}{l} \quad (40)$$

This equation shows the relationship between quantum yield ( $\phi$ ) and reductant concentration  $[AH_2]$  i.e.  $l$ .

The inverse of the quantum yield from equation (31) can now be written as:

$$\frac{\alpha}{2} \cdot \frac{1}{\phi} = \frac{k_5}{K_1 (k_8 + k_{22} K_2 A)} \cdot \frac{1}{h_0} + \frac{k_6}{K_1 h_0 (k_8 + k_{22} K_2 A) l} + \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A}{k_8 l + k_{22} K_2 l A} \quad (41)$$

( $k_7$  and  $k_{12}$  terms have been neglected).

Equation (41) shows the relationship between  $1/\phi$  and  $1/h_0$ . The ratio  $k_5/K_1(k_8 + k_{22}k_2A)$  was obtained through from the slope of plots given in Fig.4.

### Determination of ratios of rate constants of the proposed reaction mechanism:

The intercepts and slopes of the plots of  $1/\phi$  vs.  $1/[AH_2]$ ,  $1/\phi$  vs.  $1/h_0$  and  $(\phi_1 - \phi)/(\phi - \phi_2)$  vs.  $1/h_0$  were calculated from the plots drawn in Figs. 2, 4 and 5 respectively. The values of intercepts and slopes are tabulated in Table 3. The ratios of various rate constants were calculated and summarized in Table 4.

**Table 3.** Intercepts and Slopes of Plots

Plots of $1/\phi$ vs $1/[AH_2]$		
$H_0$	Intercept	$10^2 \times$ Slope
4.02	3.50	4.50
7.37	5.75	5.85
Plots of $1/\phi$ vs $1/h_0$		
$[AH_2]$	Intercept	$10^5 \times$ Slope
$1.0 \times 10^{-3}$	9.70	6.60
$1.0 \times 10^{-2}$	5.85	2.00
Plots of $(\phi_1 - \phi) / (\phi - \phi_2)$ vs $1/h_0$		
$[AH_2]$		$10^5 \times$ Slope
$1.0 \times 10^{-3}$		0.95
$1.0 \times 10^{-2}$		1.82

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Reductant: Dimethylamine

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**Table 4.**  
RATIOS OF RATE CONSTANTS

Ratios of rate constants	Values of dimethylamine
$k_6/(K_1.k_{13})$	$1.46 \times 10^{-3}$
$k_7/(k_6 + k_8)$	$1.02 \times 10^{-2}$
$k_{13}/(k_9 + k_{10} + k_{12}K_2 + k_{14}K_2A)$	$1.28 \times 10^{-2}$
$2(k_6 + k_8)/\alpha \cdot k_8$	5.75
$2k_7/\alpha \cdot k_8$	$5.85 \times 10^{-2}$
$2k_{13}/\alpha \cdot (k_9 + k_{23}K_2A)$	$4.50 \times 10^{-2}$
$2(k_9 + k_{10} + k_{12}K_2 + k_{14}K_2A)/\alpha \cdot (k_9 + k_{23}K_2A)$	3.50
$2k_6/\alpha \cdot K_1(k_9 + k_{23}K_2A)$	$6.60 \times 10^{-5}$ at low $[AH_2]$
	$2.00 \times 10^{-5}$ at high $[AH_2]$
$(k_6 + k_8)/K_1(k_9 + k_{10} + k_{12}K_2 + k_{14}K_2A)$	$9.50 \times 10^{-6}$ at low $[AH_2]$
	$1.82 \times 10^{-5}$ at high $[AH_2]$

The ratios of  $k_6/k_7$  and  $(k_5/k_7)/k_7$  as mentioned in equation (40) were calculated from the slopes and intercepts of the plots between  $1/\phi$  and  $1/[AH_2]$  as shown in Fig. 2 at low acidity. In these ratios  $k_5$  and  $k_6$  correspond to the rate constants of deexcitation of triplet excited states of thionine and only  $k_7$  is responsible to form a reduced state of thionine, i.e., semithionine.

The ratio  $\frac{k_8l+k_9l+k_{10}+k_{11}K_2l+k_{12}+k_{13}K_2lA}{k_8l+k_{12}+k_{22}K_2lA}$  was obtained through the

intercept of a graph plotted between  $1/\phi$  and  $1/[AH_2]$  as shown in Fig. 2. In this ratio as values of  $k_{10}$  and  $k_{12}$  are neglected, the ratio becomes  $(k_8 + k_9 + k_{11}K_2 + k_{13}K_2A)/(k_8 + k_{22}K_2A)$ . In this ratio,  $k_{22}$  is the sum of the two rate constants i.e.  $k_{14}$  and  $k_{15}$  which are very important because of involvement of the complex  ${}^3T.H_2^{++} \cdot AH_2$ . The rate constant  $k_{11}$  has a retardation effect in the mechanism as it controls the association of the complex  ${}^3TH_2^{++} \cdot AH_2$ . The rate constant  $k_{11}$  also has a retardation effect on quantum yield in the mechanism as it involves the dissociation of the complex  ${}^3T.H_2^{++} \cdot AH_2$ . The  $k_9$  has little effect because of lesser chance of thionine triplet state to be reexcited by releasing thermal heat.  $k_8$  is associated with the conversion of protonated triplet state of thionine into protonated state of semithionine. In general, it is assumed that the ratio  $(k_8 + k_9 + k_{11}K_2 + k_{13}K_2A)/(k_8 + k_{22}K_2A)$  plays a very significant role in controlling the quantum yield in the region of high acidity.

Using equation (38), the value of the ratio  $(k_{12})/(k_8 + k_{22}K_2A)$  is calculated from the slopes of plots of reciprocal of the quantum yield against the reciprocal of the concentration of dimethylamine i.e.  $1/\phi$  versus  $1/[AH_2]$  as shown in Fig.2. This ratio plays a very important role because of the involvement of  $k_{12}$ , in the presence of high acidity and low reductant concentration.

The ratios  $(k_8l + k_9l + k_{10} + k_{11}K_2l + k_{12} + k_{13}K_2lA)/(k_8l + k_{12} + K_{22}K_2lA)$ ,  $k_6/K_1h_0$ ,  $(k_8l/K_{22}K_2lA)$  and  $k_5/K_1(k_8 + k_{22}K_2A)$  were calculated from the intercepts and slopes of the plots of  $1/\phi$  versus  $1/h_0$  as shown in Fig. 4 using Equation (41). The ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  provides the base of step (4) i.e. Equation (7) of the suggested mechanism. The equilibrium constant  $K_1$  indicates the balance point between triplet excited and protonated triplet excited state of thionine. A high value of the ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  would indicate that the process of de-excitation of the triplet state of thionine is predominant over the other processes leading to the formation of semithionine and leucothionine. Similarly a low value of the ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  would suggest that the reduction of thionine into semithionine and leucothionine dominates over the process of de-excitation of the triplet state of thionine.

Some limitation have been applied on the very complicated ratios such as

$(k_8l + k_9l + k_{10} + k_{11}K_2lA)/(k_8l + K_{22}l.AK_2)$  and  $k_6/K_1h_o (k_8l + k_{22}K_2lA)$  in order to simplify them and obtain some meaningful information. It was assumed that steps 8 and 10 (Equations 11 and 13) are extremely slow, which leads to the conclusion that the de-excitation of the  ${}^3TH^+$  and  ${}^3TH_2^{++}$  species is not taking place by releasing thermal energy. Therefore, the rate constants  $k_6$  and  $k_{10}$  are neglected and the above ratio is reduced to  $(k_8 + k_9 + k_{11}K_2A)/(k_8 + k_{22}AK_2)$ . In this ratio, the equilibrium constant  $k_2$  and rate constants  $k_{11}$ ,  $k_{13}$  and  $k_{22}$  are associated with the formation and the consumption of a weakly associated complex of thionine triplet state and reductant molecules. This ratio shows the contribution of the complex ( ${}^3TH_2^{++} \cdot AH_2$ ) to the quantum yield of this photochemical reaction.

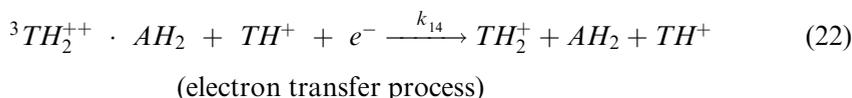
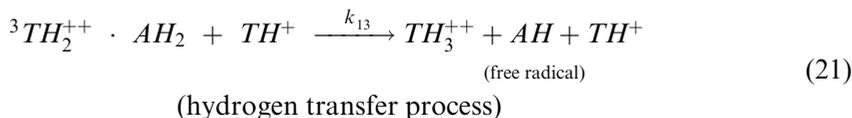
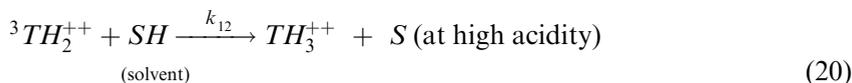
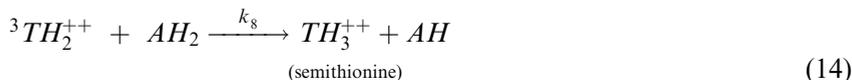
Using Equation (37), the ratio  $(k_5l + k_7l + k_6)/K_1(k_8l + k_9l + k_{10} + k_{11}K_2l + k_{12} + k_{13}K_2lA)h_o$  was calculated from the slopes of the plot between  $(\phi_1 - \phi)/(\phi - \phi_2)$  versus  $1/h_o$  as shown in Fig. 5. This ratio can be simplified by fixing some limitations and neglecting some less important rate constants. Here it is assumed that the de-excitation through thermal energy is not taking place up to detectable limits. Therefore, the rate constants  $k_6$  and  $k_{10}$  can be neglected. Since  $k_{12}$  is very small as compared to sum of other terms in the denominator of the ratio,  $k_{12}$  can easily be neglected without changing the quantity of the ratio. Therefore after neglecting  $k_6$ ,  $k_{10}$  and  $k_{12}$ , the above ratio is reduced to:  $(k_5 + k_7)/K_1 (k_8 + k_9 + k_{11}K_2 + k_{13}K_2A)$ . In this ratio  $k_7$  is associated with the formation of semithionine through the singly protonated triplet state of thionine, while in specific rate constants  $k_8$  and  $k_{13}$ , the doubly protonated triplet states of thionine are involved. Therefore, this ratio gives some idea about the extent of the contribution of singly protonated or doubly protonated triplet states of thionine in the reaction mechanism of this photochemical reaction.

## CONCLUSIONS

The path of the photochemical reaction of thionine consists of four main steps:

- (i) reaction of protonated thionine in the triplet excited state with a reductant molecule, forming semithionine,
- (ii) conversion of the protonated triplet state of thionine into semithionine by taking a hydrogen atom from a solvent molecule,
- (iii) conversion of a protonated triplet excited thionine-reductant complex into semithionine through a free radical transfer process, and
- (iv) conversion of a protonated triplet excited thionine-reductant complex into semithionine through an electron transfer process.

These steps are given below:



The quenching of the complex with unexcited thionine cation requires some activation energy.

The conclusions obtained from our results agree with the available literature data. The triplet excited state of thionine which was supposed to react with the reductant is also reported by Faure *et al.* (1967). This shows that fluorescence of thionine is not quenched when a photochemical reaction is occurring. Therefore, it was concluded that the reacting excited state is the triplet state.

The conclusion that  ${}^3Th H_2^{++}$  associates with reductant ( $AH_2$ ) forming a thionine - reductant complex is also supported by the results of Fahimuddin (2000). The presence of unexcited thionine the complex by electron transfer oxidation reduction process produces semithionine and leucothionine which was also confirmed by Bonneau *et al.* (1974) and Bonneau & Pereyre (1975). This indicates that the semireduced form of thionine modifies the rate of bimolecular disappearance of transient.

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## اختزال الثيونين الكيميائي الضوئي بواسطة الأمين ثنائي الميثيل

فهيم الدين و قاضي ظهير الحسين

قسم الكيمياء - جامعة كراتشي

### خلاصة

أُجريت هذه الدراسة باستخدام جهاز صمم خصيصاً لهذا الغرض .

وقد تمت تلك التفاعلات في وسط مائي بوجود الكحول الميثيلي بنسبة حجمين قدرها 50% وعند درجة حرارة  $25 \pm 0.1^\circ\text{C}$  وباستخدام محاليل الإيستندات المنظمة تم تحديد حمضيته المحاليل قيد الدراسة .

وبتغير تراكيز كل من الثيونين والأمين ثنائي الميثيل تمكنا من تقدير الناتج الكمي ( $\phi$ ) لتلك التفاعلات الكيميائية الضوئية . ووفقاً لميكانيكية التفاعل ، تم تفسير النتائج التي تم الحصول عليها . وبناء عليه فإن قيم الناتج الكمي ( $\phi$ ) تتغير وفقاً لكل من :

(i) الحمضية (ii) تركيز المادة المختزلة  $[AH_2]$

ونستخلص ذلك أن تفاعلات الثيونين مع الأمين ثنائي الميثيل يتم التحكم بها من خلال نوعين من الاتزان فيما بينهما :

(i) الحالة الثلاثية الخاصة بالثيونين  $[3TH^+]$  مع أيون الهيدروجين والحالة الثلاثية للثيونين المزودة بأيون هيدروجيني  $[^3T.H_2^+]$  .

(ii) الحالة الثلاثية للثيونين المزودة بأيون هيدروجين مع المادة المختزلة والمترابك الناتج عن اتحاد الثيونين بالمادة المختزلة  $[^3T.H_2^+.AH_2]$  .