

## PHOTOREDUCTION OF THIAZINE DYE WITH TRIMETHYLAMINE

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### الخلاصة :

نستقصي في هذا البحث صيغة الثيونين وتفاعلها الضوئيكيميائي مع التراي ميثيل - أمين المخفف. أُجريت هذه التفاعلات في خلية صُمِّمَتْ خصيصاً لهذا الغرض بحيث تمكننا من التحكم في درجة الحرارة. قيسَ الضوء النافذ بواسطة فرق الجهد الناتج باستخدام جلفانوميتر. تم التحكم في درجة الحموضة باستخدام الأسيتيت ومن ثم قيست درجة الحموضة بطريقة المطيافية بدلالة اقتران هاميت للحموضة ( $H_0$ ) كما أنه أمكن تمثيل الناتج الكمي ( $\Phi$ ) بواسطة الاقتران ( $H_0$ ) وتركيز المادة المستخدمة ( $AH_2$ ) في حين وجدنا أن  $\Phi$  لا يعتمد على تركيز الصيغة المستخدمة.

نقترح في هذا البحث نمطية مُعَيَّنَة لتفسير هذه النتائج بحيث يُمكن حساب ثوابت النسب لهذه النمطية. توصلنا إلى أن حالة الإثارة الثلاثية للثيونين ( $Th.H_{2T}^{++}$ ) أكبر الأثر في تحديد الناتج الكمي ( $\Phi$ )، في حين كان التركيب ( $Th.H_{2T}^{++}.AH_2$ ) العامل الفاعل في تحديد نسب النواتج، ويمكن لهذا التركيب أن يتحوَّل بالنقل الالكتروني أو بنقل الأساس الحر. وجدنا أيضاً أنه يمكن التحكم بالناتج الكمي بواسطة طريقتين للاتزان: ١ - حالة الإثارة الثلاثية للثيونين مع البروتون والحالة الثلاثية البروتونية للثيونين، ٢ - الحالة الثلاثية الإثارة للثيونين مع الخافض والمركب المعقد المرافق للثيونين مع الخافض ( $Th.H_{2T}^{++}.AH_2$ ).

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## ABSTRACT

Thionine, being a typical representative of thiazine dyes, was selected for investigations of photochemical reactions with organic reductants such as trimethylamine in 50% aqueous methanol. The photochemical reduction was carried out in a specially designed apparatus provided with a double-walled temperature-controlled reaction cell. Transmitted light was observed in terms of electrical signals through calibrated galvanometers. Acidities of solutions were controlled by acetate buffers and determined by means of the spectrophotometric method in terms of Hammett acidity function ( $H_o$ ). It was observed that quantum yield ( $\phi$ ) is a function of acidity ( $H_o$ ) as well as concentration of reductant ( $AH_2$ ). The quantum yield was found to be independent of the concentration of thionine dye.

The results have been interpreted in terms of a proposed mechanism. The ratios of certain rate constants for the proposed mechanism have been evaluated. It was concluded that the protonated triplet excited state of thionine ( $Th.H_{2T}^{++}$ ) makes a major contribution to the determination of quantum yield ( $\phi$ ). The complex ( $Th.H_{2T}^{++}.AH_2$ ) is the rate controlling species and it may undergo either a electron transfer process or a free radical transfer process. It was also found that the quantum yield is controlled by two equilibria: (i) triplet excited state of thionine with proton and protonated triplet state of thionine; and (ii) protonated triplet excited state of thionine with reductant and associated complex of thionine with reductant ( $Th.H_{2T}^{++}.AH_2$ ).

## PHOTOREDUCTION OF THIAZINE DYE WITH TRIMETHYLAMINE

### INTRODUCTION

Early investigators studied the photochemical reduction of thionine with organic reductants. Their work was qualitative in nature, and they paid little attention to kinetic studies [1–8]. The organic reductants include thiourea and its substituted derivatives, anethole, glycerol, glycol, phenylhydrazine, EDTA, *etc.* Lavalliant [9] found that when the concentration of the dye increases from  $10^{-4}$  mol dm<sup>-3</sup>, the photochemical reaction became more and more difficult to occur and no photochemical reaction was observed at a concentration of  $10^{-3}$  mol dm<sup>-3</sup>. The photochemical properties of thionine covalently bound to other macromolecules were studied by Viswanathan *et al.* [10, 11]. Gilch [12] studied the electron transfer quenching of triplet methylene blue and which was found to be sensitive towards an external magnetic field. The spectrophotometric characteristics of methylene blue in different organic solvents was also studied by Feng *et al.* [13]. Soomer *et al.* [14] and Kraemer *et al.* [15] reported that photooxygenation of allylthiourea with thionine as sensitizer takes place *via* radicals at high allylthiourea concentration. Kirjak [16] examined the influence of thionine and methylene blue on the electroreduction of Bi(III) and Te(IV) in chloride and tartarate solutions. Reductimetric studies of thiazine dyes with iron(II) was carried out by Raju *et al.* [17] in buffer medium of different pH. Static fluorometric technique was adopted by Buchweiser [18] for the studies of fluorescence quenching of the protonated and unprotonated forms of thionine and neutral red by several electron donors.

The aim of the present work is to study the kinetics of photochemical reaction of thionine with reductant (trimethylamine). Effects of various parameters such as concentration of reductant [AH<sub>2</sub>], concentration of dye [Th], acidity ( $H_0$ ), and temperature ( $T$ ) on quantum yield ( $\phi$ ) are to be used in an oxygen-free atmosphere. Results obtained are to be used in establishing a mechanism for this photoreduction process.

### EXPERIMENTAL

A special type of apparatus was constructed in order to meet the requirement of photochemical reaction of thionine. The apparatus consists of the following systems: (i) light source (a mercury vapor high pressure source of light from a Mazda box type lamp 200–250 V), (ii) optical system for parallel beam, (iii) monochromating system, (iv) double walled reaction cell, (v) magnetic stirring system, (vi) temperature controlling system, (vii) photodetectors and signals recording systems, and (viii) Fieser's arrangement [19] for deoxygenation of nitrogen. All these systems were arranged with optical bench (as shown in Figure 1) and housed in a dark room. An optical bench was set to obtain the parallel beam of light. Light from the source was made to pass through convex lenses  $L_1$ ,  $L_2$ , and  $L_3$ . In between lenses  $L_2$  and  $L_3$  light was passed through a hole ( $O$ ) of 2 mm diameter. Filter solutions  $F_1$  and  $F_2$  were used for monochromation. A plain reflector ( $R$ ) was used for reflection of fraction of light to a reference photocell ( $P_2$ ). Remaining fraction of light was passed through reaction cell ( $C$ ). A magnetic stirrer ( $M$ ) was used. The photocell ( $P_1$ ) was used to detect the light intensity. The photocells  $P_1$  and  $P_2$  were connected to galvanometers respectively.

The monochromatic light in a narrow band from 577 nm to 579 nm was obtained by a set of filter solutions as suggested by Bowen [20]. Reaction cell is same as used by Fahimuddin *et al.* [21, 23]. This is upgraded and modified ell as compared to the cell used by previous workers [24–26]. The construction of reaction cell is shown in Figure 2. The constant temperature was obtained by a thermostatic water bath of type T-52 manufactured by Haak-Karlshure.

An analar grade thionine indicator and extra pure trimethylamine solution from E. Merck were used without further purification. The molar extinction coefficient of the dye in 50% aqueous methanol was calculated as  $4.7 \pm 0.5 \times 10^4$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, at 580 nm, which is very close to the value  $4.9 \times 10^4$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> at 604 nm as reported by Fahimuddin [21]. 99.8% pure nitrogen gas supplied by Pakistan Oxygen Ltd. was used. Traces of oxygen were also removed by the method described by Feiser [19]. Extra pure quality of indicator acridine orange, sodium hydroxide, sodium hydrogen sulfate, sodium anthroquinone-2-sulfonate, lead acetate, sodium acetate, hydrochloric acid, cupric chloride, potassium dichromate, sulfuric acid, calcium chloride, and oxalic acid from E. Merck were used. Stock solutions of thionine, trimethylamine, and others were prepared in 50% aqueous methanol and kept in polyethylene bottles.

The intensity of light ( $I_0$ ) was measured using the following relation:

$$I_0 = 3.559 \times 10^{-6} \cdot x \text{ Einstein per second}$$

where  $x = x_1 - x_2$  (where  $x_1$  is the galvanometer reading with no light striking the photocell and  $x_2$  is the reading of galvanometer when the photocell is exposed to light).

An optical method was adopted using acridine as a basic indicator for the determination of acidity of reaction solution as described earlier by Fahimuddin [21]. Acidity of solution ( $H_0$ ) was determined using the following relationship:

$$H_0 = pk_a - \log \frac{d_1 - d_2}{d - d_2}$$

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

Reaction mixtures consisting of calculated volumes of thionine solution, reductant, and acetate buffer solutions were pipetted out into 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 of nitrogen, the bubbler was lifted up and the flow of nitrogen over the surface of solution was maintained during the irradiation. The lamp was on 30 minutes earlier than irradiation process. Photocell responses were noted with no cell in beam ( $D_0$ ), with the cell containing solvent ( $D_m$ ) and the cell containing reaction mixture ( $D_{nt}$ ). Observations on reference galvanometer were also noted.  $H_0$  values were measured in duplicate portion of reaction solution during the flushing period.

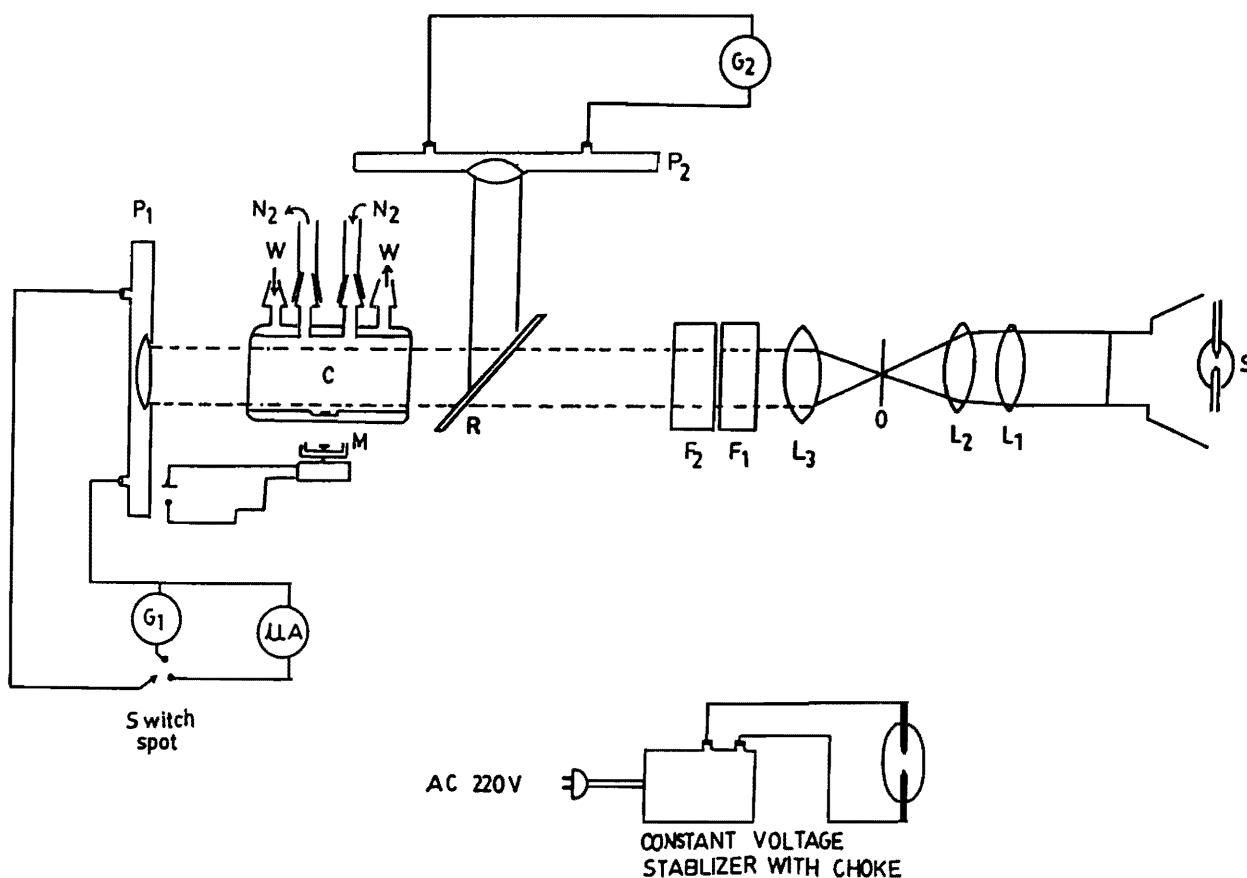


Figure 1. The optical bench.

**RESULTS AND DISCUSSION**

Quantum yield ( $\phi$ ) is defined as number of dye molecules of reactants converted into products per unit Einstein of light absorbed:

$$\phi = \frac{\text{no. of thionine molecules undergo reduction per second}}{\text{no. of Einstein of light absorbed per second}}$$

The quantum yield for the reaction of thionine with trimethylamine was calculated using the following relationship:

$$\log \left( \frac{D_m - D_{nt}}{D_{nt}} \right) = \frac{I_o \cdot (1 - \alpha) \cdot \epsilon \cdot \phi \cdot L \cdot t}{2.303V} + \log \frac{D_m - D_{ni}}{D_{ni}}$$

where  $D_{ni}$  is the deflection for the reaction mixture in the cell at initial condition;  $\alpha$ , the fraction of light lost at each window;  $\epsilon$ , the molar extinction coefficient for thionine in 50% aqueous methanol at 605 nm, was

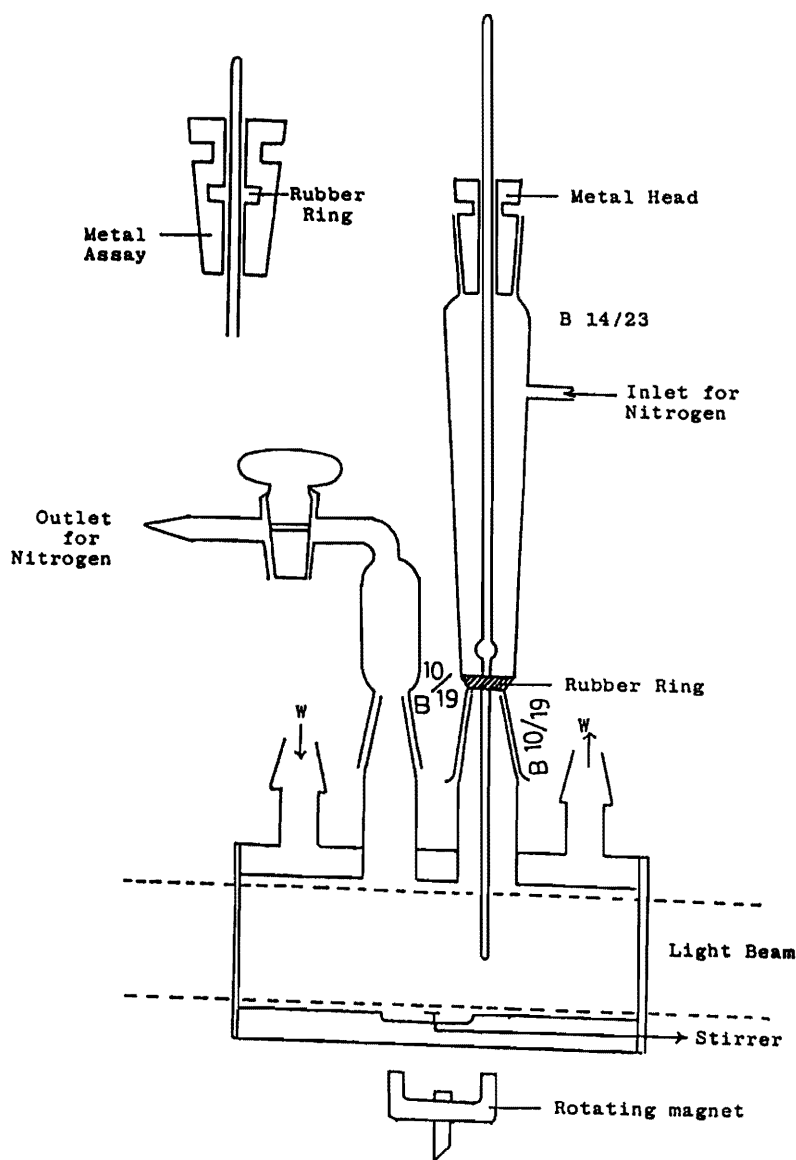


Figure 2. The reaction cell.

$4.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ;  $L$ , the length of the path travelled by the beam in the cell, was 6.0 cm;  $V$ , the volume of the solution =  $0.0250 \text{ dm}^3$ .  $I_0$  and  $\alpha$  were measured during the experiment.

Calculated volume of dye and reductant were pipetted out into the reaction cell and added with acetate buffer to keep  $H_0$  constant. The inert condition of reaction mixture was obtained by bubbling oxygen free dry nitrogen through the solution for forty minutes. A comparative study to prove the importance of nitrogen bubbling for more than 10 minutes is given in Table 1. It was observed that time for flushing of nitrogen is very important for reduction of thionine with trimethylamine and it proves that 30 minutes flushing time for nitrogen is quite satisfactory for inert condition in the reaction cell. In this present work, nitrogen was bubbled for 40 minutes before each run.

The influence of acidity on photochemical reduction of thionine with trimethylamine was studied by varying  $H_0$  range from 3.53 to 7.64. The concentration of thionine was same for all the experiments. Acidity and quantum yield data are presented in Table 2. It was observed that quantum yield decreases when the value of  $H_0$  increases. This dependency of

**Table 1. Quantum Yield-Time for Nitrogen Bubbling.**

$10^6$ [Thionine] (mol.dm <sup>-3</sup> )	$10^2$ [Trimethylamine] (mol.dm <sup>-3</sup> )	Time for N <sub>2</sub> bubbling (s) (minutes)	$10 \phi$
2.0	1.0	10	0.18
2.0	1.0	20	0.18
2.0	1.0	30	0.80
2.0	1.0	40	0.88
2.0	1.0	60	0.89

**Table 2. Effect of Variation of Acidity on the Quantum Yield of the Reaction Between Thionine and Trimethylamine.**

[Th]: $2.0 \times 10^{-6} \text{ mol.dm}^{-3}$		Temperature: 25°C	
AH <sub>2</sub> : Trimethylamine		Solvent: 50% Aqueous Methanol	
Buffer: Acetate			
$H_0$	$\phi$	$10^{-1}/\phi$	$10^{-6}/h_0$
[AH <sub>2</sub> ] = $1.0 \times 10^{-2} \text{ mol.dm}^{-3}$			
3.53	0.220	0.454	0.003
4.02	0.199	0.502	0.010
4.25	0.198	0.505	0.018
5.16	0.148	0.676	0.144
6.88	0.103	0.971	7.585
7.37	0.094	1.020	23.442
7.64	0.088	1.136	43.650
[AH <sub>2</sub> ] = $1.0 \times 10^{-3} \text{ mol.dm}^{-3}$			
3.53	0.110	0.909	0.003
4.02	0.108	0.926	0.010
4.25	0.106	0.943	0.018
5.16	0.094	1.064	0.144
6.88	0.064	1.562	7.585
7.37	0.061	1.639	23.442
7.64	0.060	1.666	43.650

quantum yield on acidity can also be observed through the plot given in Figure 3. The plot of  $1/\phi$  against  $1/h_o$  is a straight line graph as shown in Figure 4. The ratios  $\frac{\phi_1 - \phi}{\phi - \phi_2}$  were plotted against  $1/h_o$  and straight lines were obtained passing through the origin as shown in Figure 5. Here  $\phi_1$  and  $\phi_2$  represent the extreme values of quantum yields at low and high acidities respectively.

The effect of the variation of reductant concentration on quantum yield of the photochemical reduction of thionine was studied by performing the experiments at different concentration of trimethylamine. The acetate buffer was used to control the acidity. The  $[AH_2]-\phi$  data obtained are summarized in Table 3. Results show that the quantum yield is increased by increasing the concentration of trimethylamine. The plots of  $1/\phi$  against  $1/[AH_2]$  are shown in Figure 6. The values of quantum yields ( $\phi$ ) obtained from the above plots at infinite concentration of trimethylamine at  $H_o = 4.02$  and  $H_o = 7.37$  are 0.348 and 0.227 respectively.

In order to study the effect of thionine concentration on quantum yield, the experiments were performed at various concentrations of thionine while all other parameters like temperature, acidity, and trimethylamine concentration were kept unchanged in all sets of experiments. The results are presented in Table 4. The results show that quantum yield is independent of the concentration of thionine. Matsumoto [27], also found that quantum yield is practically independent of the dye (methylene blue concentration) in the  $(1-5) \times 10^{-6}$  mol dm<sup>-3</sup> range at a fixed value of pH=7.0 with parachlorophenylglycine of concentration  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>. Fahimuddin *et al.* [21] also reported that quantum yield is independent of the concentration of thionine with *N*-phenylglycine in absolute methanol.

The temperature dependency of the photoreduction of thionine was studied by performing the experiments at different temperatures ranges from 15°C to 35°C. The data are given in Table 5. The results show that quantum yield increases by

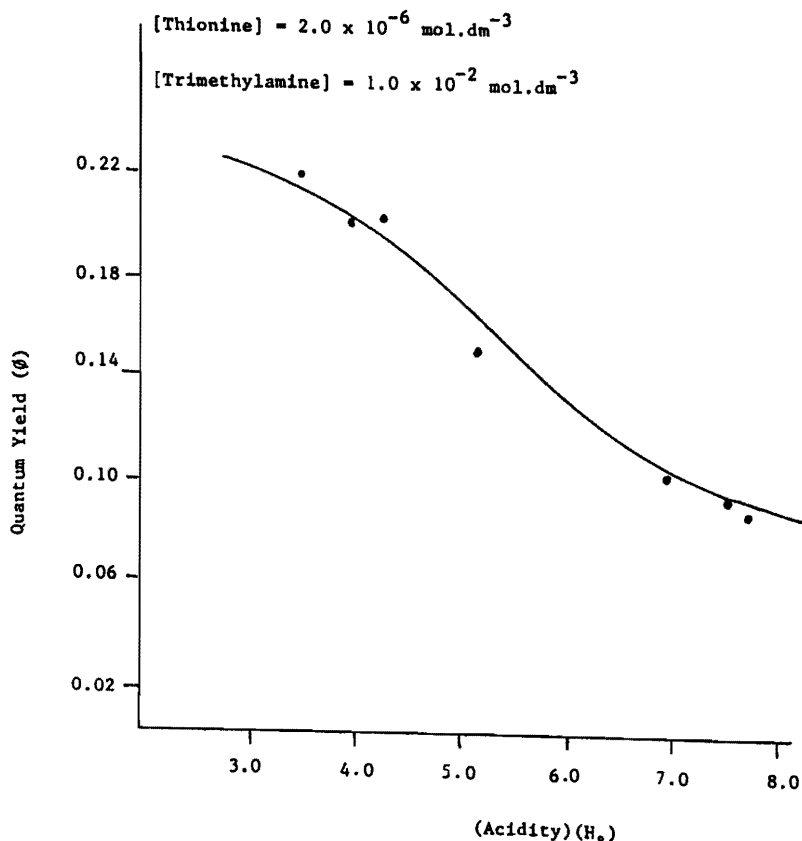


Figure 3. Plot of  $\phi$  versus  $H_o$ .

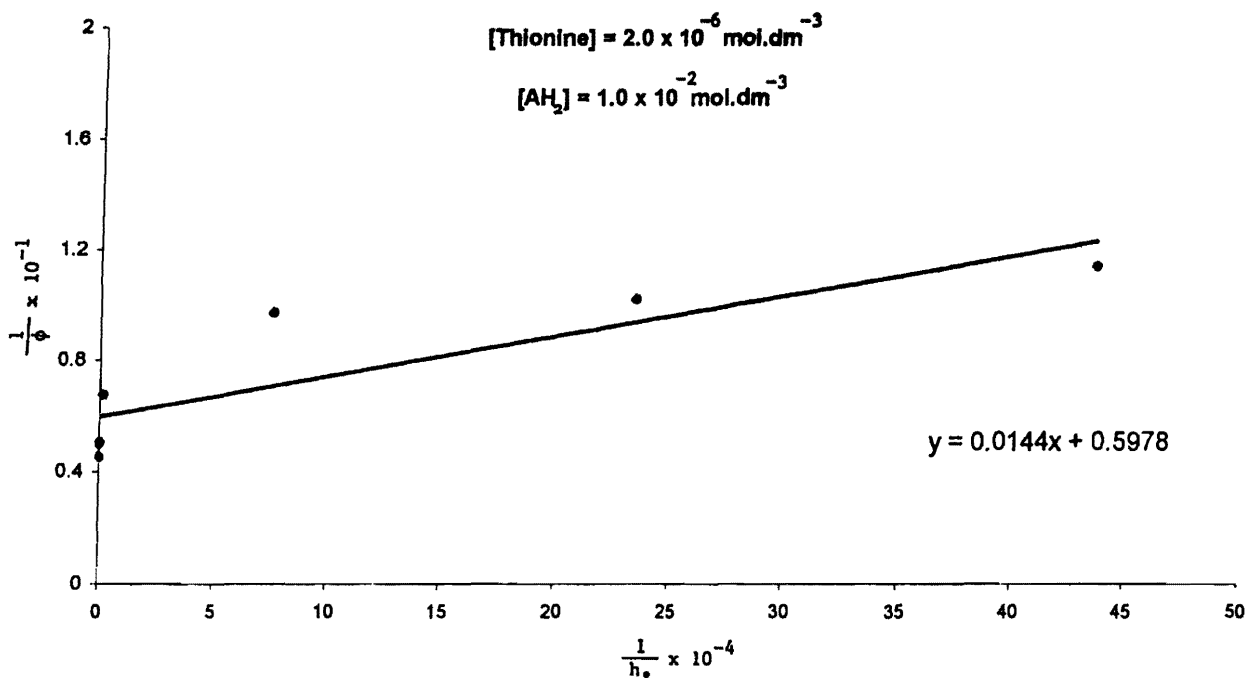


Figure 4. Plot of  $\frac{1}{\phi}$  versus  $\frac{1}{h_o}$ .

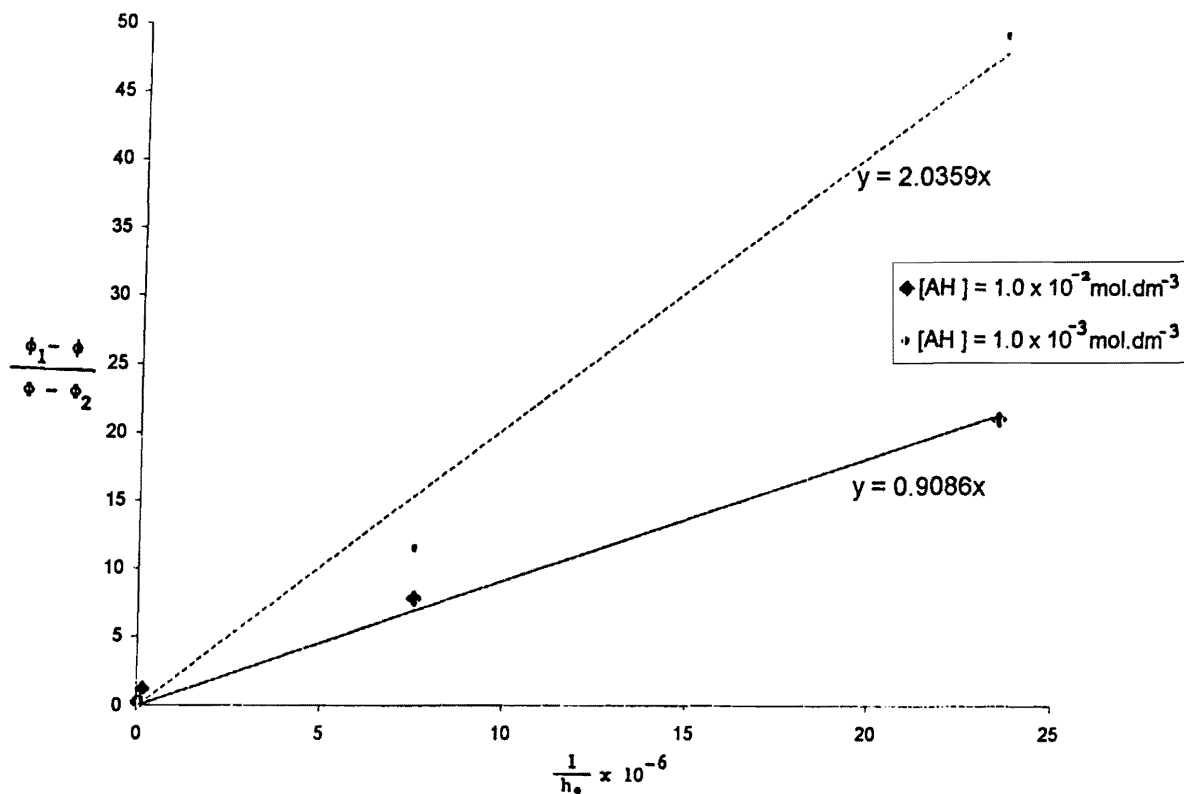
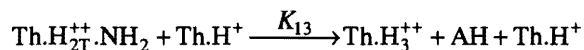


Figure 5. Plot of  $\left(\frac{\phi_1 - \phi}{\phi - \phi_2}\right)$  versus  $\frac{1}{h_o}$ .



increasing temperature. The values of temperature coefficients for five degree rise in temperature were also evaluated and tabulated in Table 5. The average value for temperature coefficient was found to be 1.147. These results are in agreement with those of Kostryukova [28] reported earlier for thionine–thionine and thionine–glucose systems. The quantum yield of the reactions of thionine with trimethylamine was found to increase with the increase in temperature. It seems, therefore the reaction



requires some activation energy.

The experimental data reveals that the process of photochemical reduction of thionine is influenced by three parameters *i.e.* acidity, concentration of reductant (trimethylamine), and temperature in which the effect of acidity is very important. It is apparently looked that the hydrogen ion plays a very vital role in the step which results in the formation of products. The plots of  $\phi$  versus  $H_o$  show that the maximum quantum yield was obtained at a minimum value of  $H_o$ . Generally, it was observed that quantum yield decreases as  $H_o$  value rises. The maximum depression in quantum yield was observed in the region 4.25 to 6.5 of  $H_o$ . Plots of  $\frac{\phi_1 - \phi}{\phi - \phi_2}$  against  $1/h_o$  show that the slopes are function of reductant concentration. Quantum yield is not affected by changing the concentration of dye. This observation is in agreement of the works of Ahmad [26] and Matsumoto [27], and it helps in setting the new mechanism in which less emphasis will be given on dye as compared to the hydrogen ion activity.

On the basis of data obtained, a general mechanism of the reaction of thionine with trimethylamine has been proposed. This proposed mechanism consists of the following steps.

**Table 3. Effect of Variation of Concentration of Trimethylamine on the Quantum Yield of Photochemical Reduction of Thionine.**

[Th]: $4.0 \times 10^{-6}$ mol dm <sup>-3</sup>		Temperature: 25°C	
AH <sub>2</sub> : Trimethylamine		Solvent: 50% Aqueous Methanol	
$10^2 \cdot [\text{AH}_2]$ (mol dm <sup>-3</sup> )	$\phi$	$10^{-2}/[\text{AH}_2]$ (dm <sup>3</sup> /mol.)	$10^{-1}/\phi$
$H_o = 4.02$			
0.1	0.091	10.00	1.10
0.4	0.094	2.50	1.06
1.0	0.148	1.00	0.68
1.6	0.208	0.62	0.48
2.4	0.238	0.42	0.42
3.2	0.270	0.31	0.37
8.0	0.283	0.12	0.35
$H_o = 7.37$			
0.1	0.071	10.00	1.41
0.4	0.073	2.50	1.37
0.8	0.106	1.25	0.94
1.2	0.114	0.83	0.88
2.0	0.132	0.50	0.76
3.2	0.176	0.31	0.57
8.0	0.201	0.12	0.50

**Table 4. Effect of Concentration of Thionine on the Quantum Yield of Photoreduction of Thionine.**

$H_0$ :	4.02	Temperature:	25°C
$[AH_2]$ :	$1.6 \times 10^{-3} \text{ mol dm}^{-3}$	Solvent:	50% Aqueous Methanol
	$[Th] \times 10^6$		$\phi$
	$\text{mol dm}^{-3}$		(With Trimethylamine)
	1.0		0.099
	2.0		0.099
	2.5		0.101
	3.0		0.100
	3.5		0.101

**Table 5. Effect of Temperature on the Quantum Yield of Photoreduction of Thionine with Trimethylamine.**

$[Thionine]$ :	$2 \times 10^{-6} \text{ mol dm}^{-3}$	Buffer:	Acetate		
$[AH_2]$ :	$1.0 \times 10^{-2} \text{ mol dm}^{-3}$	Solvent:	50% Aqueous methanol		
$H_0$ :	4.02				
	Temperature (°C)				
	15	20	25	30	35
$\phi$	0.150	0.172	0.198	0.227	0.262
	$\phi_{20}/\phi_{15}$	$\phi_{25}/\phi_{20}$	$\phi_{30}/\phi_{25}$	$\phi_{35}/\phi_{30}$	
Temperature coefficient	1.15	1.15	1.14	1.15	

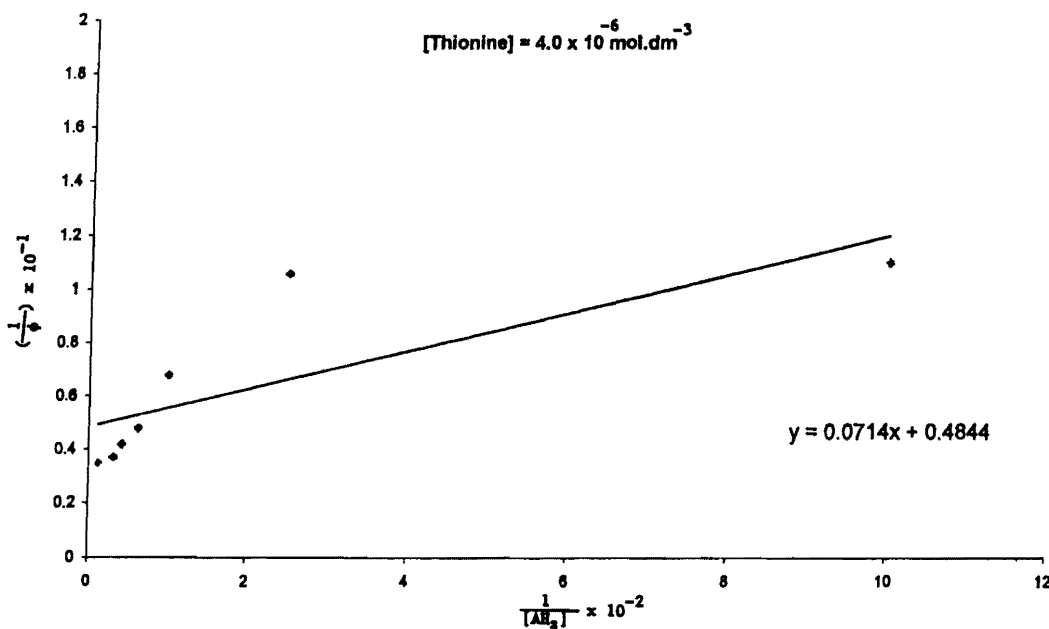


Figure 6. Plot of  $\frac{1}{\phi}$  against  $\frac{1}{[AH_2]}$ .

Excitation of thionine molecule takes place by absorbing a quantum of light and forms a singlet excited state:



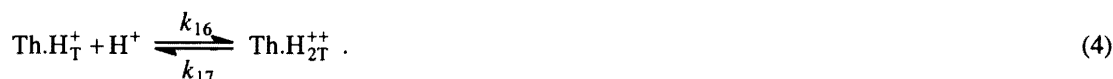
There is a chance that the excited singlet state of thionine may lose the light, energy in the form of fluorescence and goes back to ground state:



The second possibility is that the singlet excited state may transfer into triplet excited state:



At high acidity, the triplet excited state combines with hydrogen ion which undergoes a reversible process:



At equilibrium:

$$K_1 = \frac{k_{16}}{k_{17}} = \frac{[\text{Th.H}_{2T}^{++}]}{[\text{Th.H}_T^+][\text{H}^+]} = \frac{[\text{Th.H}_{2T}^{++}]}{[\text{Th.H}_T^+]} \times \frac{1}{h_0} . \quad (5)$$

De-excitation of the singlet excited state and triplet excited state may occur either by colliding with an other thionine molecule or with a reductant molecule. The steps of de-excitation are written as:



The triplet excited state may simply transfer into ground state by releasing thermal energy:



The triplet excited state and protonated triplet excited state are supposed to react with reductant from semithionine:



The protonated triplet excited state may undergo de-excitation either by colliding with the reductant molecule or by simply releasing thermal heat to the system.



The protonated triplet excited state may associate with reductant molecule:



$$K_2 = \frac{k_{18}}{k_{19}} = \frac{[\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2]}{[\text{Th.H}_{2\text{T}}^{++}][\text{AH}_2]} .$$

This complex may dissociate by losing its energy:

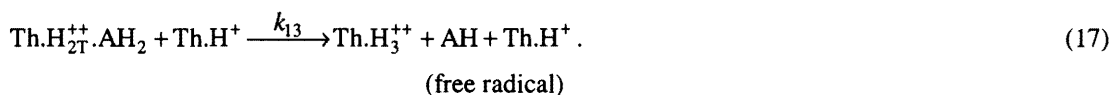


This process is supposed to occur at low acidity (at high value of  $H_0$ ).

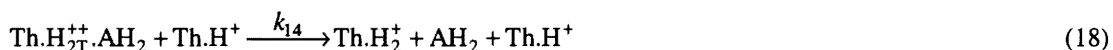
The role of solvent, as investigated by Ahmad [25] is considered very prominent in region of high acidity (at low value of  $H_0$ ):



The triplet–thionine–reductant complex may undergo an oxidation–reduction process within the two parts of the complex when it strikes the unexcited radical of thionine through a hydrogen transfer process:



The oxidation–reduction reaction may occur in the above complex by an electron transfer process also:



Semithionine ( $\text{Th.H}_3^{++}$ ) on disproportionation gives leucothionine ( $\text{Th.H}_4^{++}$ ):



This reaction is supposed to occur in region of low acidity. The free radicals of reductant may undergo the termination process:



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

Let  $[I]_a$  be the quanta of light absorbed and calculated by adding rate equations of the proposed mechanism:

$$\begin{aligned} [I]_a = & k_5 [\text{Th.H}_1^+][\text{AH}_2] + k_6 [\text{Th.H}_1^+] + k_7 [\text{Th.H}_1^+][\text{AH}_2] + \\ & k_8 [\text{Th.H}_{2\text{T}}^{++}][\text{AH}_2] + k_9 [\text{Th.H}_{2\text{T}}^{++}][\text{AH}_2] + k_{10} [\text{Th.H}_{2\text{T}}^{++}] + \\ & k_{11} [\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2] + k_{12} [\text{Th.H}_{2\text{T}}^{++}] + k_{13} [\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2][\text{Th.H}^+] . \end{aligned} \quad (22)$$

Thionine radical after reduction converts into semithionine and leucothionine. The rate of reduction of the process is equal to the rate of disappearance of thionine.

$$-\frac{d[\text{Th.H}^+]}{dt} = \frac{1}{2} \left\{ \frac{k_7 [\text{Th.H}_1^+][\text{AH}_2] + k_8 [\text{Th.H}_{2\text{T}}^{++}][\text{AH}_2] + k_{12} [\text{Th.H}_{2\text{T}}^{++}]}{k_{13} [\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2][\text{Th.H}^+] + k_{14} [\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2][\text{Th.H}^+]} \right\} . \quad (23)$$

Suppose that

$$[\text{Th.H}_1^+] = a, [\text{Th.H}_{2\text{T}}^{++}] = b, [\text{Th.H}_{2\text{T}}^{++}.\text{AH}_2] = c, [\text{Th.H}^+] = A, [\text{AH}_2] = l, \text{ and } [\text{H}^+] = h_0$$

substituting these symbols in Equation (22) and (23):

$$\alpha[I]_a = k_5al + k_6a + k_7al + k_8bl + k_9bl + k_{10}b + k_{11}c + k_{12}b + k_{13}cA \quad (24)$$

$$-\frac{d[\text{Th.H}^+]}{dt} = \frac{1}{2} [k_7al + k_8bl + k_{12}b + (k_{13} + k_{14})cA]. \quad (25)$$

The sum of the constant terms  $k_{13}$  and  $k_{14}$  is equal to  $k_{22}$ . Therefore, Equation (25) becomes:

$$-\frac{d[\text{ThH}^+]}{dt} = \frac{1}{2} [k_7al + k_8bl + k_{12}b + k_{22}cA]. \quad (26)$$

The quantum yield of the photochemical reaction is represented as:

$$\phi = \frac{-\frac{d[\text{ThH}^+]}{dt}}{[I]_a} \quad (27)$$

$$\phi = \frac{\alpha}{2} \cdot \frac{k_7al + k_8bl + k_{12}b + k_{22}cA}{k_5al + k_6a + k_7al + k_8bl + k_9bl + k_{10}b + k_{11}c + k_{12}b + k_{13}cA} \quad (28)$$

Again refer to the Equations (4) and (14) which give:

$$b = K_1 ah_o \text{ and } c = K_2 bl \text{ or } c = K_1 K_2 ah_o l. \quad (29)$$

Substituting values of  $b$  and  $c$  in Equation (28):

$$\phi = \frac{\alpha}{2} \cdot \frac{lk_7 + K_1 h_o (k_8l + k_{12}) + k_{22} K_1 K_2 h_o \cdot Al}{k_5l + k_6 + k_7l + K_1 h_o (k_8l + k_9l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 lA)} \quad (30)$$

at high  $h_o$ , the  $\phi = \phi_1$ .

At high acidity, the species  $[\text{ThH}_T^+]$  is not supposed to be present, therefore, the steps involving  $[\text{ThH}_T^+]$  have been neglected and Equation (30) reduces to:

$$\phi_1 = \frac{\alpha}{2} \cdot \frac{K_1 h_o (k_8l + k_{12} + k_{22} K_2 lA)}{K_1 h_o (k_8l + k_9l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 lA)} \quad (31)$$

when  $l = 0$ , then

$$\phi_1(\text{Solvent}) = \frac{\alpha}{2} \cdot \frac{k_{12}}{(k_{10} + k_{12})} \quad (32)$$

at low  $h_o$   $\phi = \phi_2$ .

At low acidity the species  $[\text{ThH}_{2T}^{++}]$  and  $[\text{ThH}_{2T}^{++} \cdot \text{AH}_2]$  are not prominent. Therefore, steps involving these two species are eliminated. Then Equation (28) reduces to:

$$\phi_2 = \frac{\alpha}{2} \cdot \frac{k_7l}{(k_5l + k_6 + k_7l)} \quad (33)$$

With the help of Equations (30), (31), and (33), the relationship between  $(\phi_1 - \phi)/(\phi - \phi_2)$  and  $h_o$  is determined as follows:

$$\frac{\phi_1 - \phi}{\phi - \phi_2} = \frac{k_6l + k_7l + k_6}{h_o K_1 (k_8l + k_9l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 lA)} \quad (34)$$

The plot of this Equation is a straight line passing through origin.

Again considering Equation (31):

$$\frac{\alpha}{2} \cdot \frac{1}{\phi_1} = \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A}{k_8 l + k_{12} + k_{22} K_2 l A} + \frac{k_{12}}{k_8 l + k_{12} + k_{22} K_2 l A} \quad (35)$$

On neglecting  $k_{12}$  from denominator:

$$\frac{1}{\phi_1} \cdot \frac{\alpha}{2} = \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{13} K_2 l A}{k_8 l + k_{22} K_2 l A} + \frac{k_{12}}{k_8 l + k_{22} K_2 l A} \cdot \frac{1}{l} \quad (36)$$

This is a straight line equation having both slope and intercept.

Again considering Equation (33):

$$\frac{\alpha}{2} \cdot \frac{1}{\phi_2} = \frac{(k_5 l + k_7 l + k_6)}{k_7 l} = \frac{(k_5 + k_7)}{k_7} + \frac{k_6}{k_7} + \frac{1}{l} \quad (37)$$

This equation shows the relationship between  $\phi$  and reductant concentration *i.e.*  $l$ .

Again referring Equation (30), neglecting  $k_7$  and  $k_{12}$  and then inverse of this equation:

$$\frac{\alpha}{2} \cdot \frac{1}{\phi} = \frac{k_8 l + k_9 l + k_{10} + k_{11} K_2 l + k_{12} + k_{13} K_2 l A}{k_8 l + k_{22} K_2 l A} + \frac{k_6}{K_1 h_o (k_8 + k_{22} K_2 A) l} + \frac{k_6}{K_1 (k_8 k_{22} K_2 A)} \cdot \frac{1}{h_o} \quad (38)$$

Equation (38) shows the relationship between  $1/\phi$  and  $1/h_o$ . The ratio  $\{k_5/K_1(k_8 + k_{22}K_2A)\}$  is obtained through slope of plots given in Figure 4.

The intercepts and slopes of plots of  $1/\phi$  vs  $1/h_o$ ,  $\phi_1 - \phi / \phi - \phi_2$  vs  $1/h_o$  and  $1/\phi$  vs  $1/[AH_2]$  were calculated from the plots drawn in Figures 4, 5, and 6 respectively. These values of intercepts and slopes are shown in Table 6. The values of various ratios of the rate constants were calculated and are summarized in Table 7.

**Table 6. Intercepts and Slopes of Plots.**

Reductant	$H_o$	Intercept	Slope
<b>Plots of <math>1/\phi</math> versus <math>1/[AH_2]</math></b>			
Trimethylamine	4.02	4.84	$7.14 \times 10^{-3}$
	7.37	7.46	$7.78 \times 10^{-3}$
<b>Plots of <math>1/\phi</math> versus <math>1/h_o</math></b>			
[ $AH_2$ ]	Intercept	Slope	
	$1.0 \times 10^{-3}$	10.56	$1.75 \times 10^{-7}$
	$1.0 \times 10^{-2}$	5.97	$1.44 \times 10^{-7}$
<b>Plots of <math>(\phi_1 - \phi / \phi - \phi_2)</math> versus <math>1/h_o</math></b>			
Trimethylamine	[ $AH_2$ ]	---	Slope
	$1.0 \times 10^{-3}$	---	$2.03 \times 10^{-6}$
	$1.0 \times 10^{-2}$	---	$9.08 \times 10^{-7}$

The ratios  $k_6/k_7$  and  $(k_5 + k_7/k_7)$  are given in Equation (37) and calculated through the slopes and intercepts of the plots of  $1/\phi$  versus  $1/[AH_2]$  as given in Figure 6 (at low acidity). In these ratios  $k_5$  and  $k_6$  corresponds to the rate constants of de-excitation of triplet excited states of thionine and only  $k_7$  is responsible to form a reduced state of thionine, i.e., semithionine.

The ratio =  $\frac{k_9l + k_{10}l + k_{11} + k_{12}K_2l + k_{13} + k_{14}K_2lA}{k_9l + k_{13} + k_{23}K_2lA}$  was obtained through intercept of graph plotted between  $1/\phi$  and

$1/[AH_2]$  as shown in Figure 6. If values  $k_{10}$  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.  $k_{13} + k_{14}$ , which are very important because of involvement of the complex  $Th.H_{2T}^{++}.AH_2$ . The rate constant  $k_{11}$  has a retardation effect on the quantum yield in the mechanism as it is involved in the dissociation of the complex  $Th.H_{2T}^{++}.AH_2$ . The term  $k_{10}$  has little effect because of the lesser chance of thionine triplet state to be de-excited by releasing thermal heat.  $k_8$  is associated with the conversion of the protonated triplet state of thionine into the 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.

The ratio  $(k_{12})/(k_8 + k_{22}K_2A)$  is appeared in Equation (36) and its value is calculated through the slopes of plots of  $1/\phi$  versus  $1/[AH_2]$  as shown in Figure 6. This ratio because of involvement of  $k_{13}$  plays very important role in the presence of high acidity and low reductant concentration.

The ratios  $\frac{k_8l + k_9l + k_{10} + k_{11}K_2l + k_{12} + k_{13}K_2lA}{k_8l + k_{12} + k_{22}K_2lA}$ ,  $k_6/K_1h_o (k_8l + k_{22}K_2lA)$  and  $k_5/K_1 (k_8 + k_{22}K_2A)$  appeared in

Equation (38) were calculated through the intercepts and slopes of the plots between  $1/\phi$  and  $1/h_o$ , as shown in Figure 4. The ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  provides the basis for step (5) in the proposed mechanism. The equilibrium constant  $K_1$  gives the balance point between triplet excited and protonated triplet excited state of thionine. The high value of this ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  leads to the conclusion 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, the low value of ratio  $k_5/K_1(k_8 + k_{22}K_2A)$  reveals that the reduction of thionine to semithionine and leucothionine dominates over the process of de-excitation of triplet state of thionine.

Table 7. Ratios of Rate Constants.

Ratios of Rate Constants	Trimethylamine
$(k_5/K_1 k_{12})$	$2.45 \times 10^{-5}$
$(k_6/k_5 + k_7)$	$1.04 \times 10^{-3}$
$(k_{12}/k_8 + k_9 + k_{11} K_2 + k_{13} K_2A)$	$1.47 \times 10^{-3}$
$2 (k_5 + k_7)/\alpha . k_7$	7.46
$2 k_6/\alpha . k_7$	$7.78 \times 10^{-3}$
$2 k_{12}/\alpha . (k_8 + k_{22} K_2A)$	$7.14 \times 10^{-3}$
$2 (k_9 + k_9 + k_{11} K_2 + k_{13} K_2A)/(k_8 + k_{22} K_2A)$	4.84
$2 k_5/\alpha . K_1(k_8 + k_{22} K_2A)$	$1.75 \times 10^{-7}$ at low $[AH_2]$ $1.44 \times 10^{-7}$ at high $[AH_2]$
$(k_5 + k_7)/K_1 (k_8 + k_9 + k_{11} K_2 + k_{13} K_2A)$	$2.03 \times 10^{-6}$ at low $[AH_2]$ $9.08 \times 10^{-7}$ at high $[AH_2]$

The ratios  $(k_8l + k_9l + k_{10} + k_{11}K_2lA)/(k_8l + k_{22}lAK_2)$  and  $k_6/K_1 h_o (k_8l + k_{22} K_2lA)$  are very complicated. Some limitations have been applied on these ratios in order to simplify them and get some meaningful information. It was assumed that steps (9) and (11) are very slow which means that the de-excitation of  $\text{Th.H}_1^+$  and  $\text{Th.H}_{2T}^{++}$  species are not taking place by releasing thermal energy. Therefore, the rate constants  $k_7$  and  $k_{11}$  are neglected and the above said 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 weak associated complex of thionine triplet state and reductant molecule. This ratio shows the extent of contribution of the complex  $(\text{Th.H}_{2T}^{++}.\text{AH}_2)$  in the quantum yield of this photochemical reaction.

Considering Equation (34) *i.e.*:

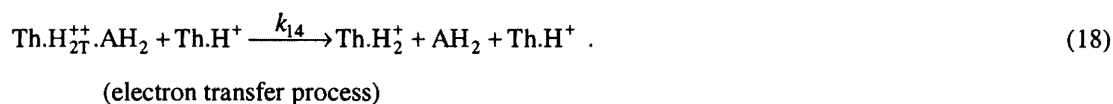
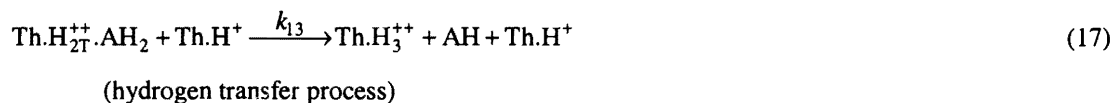
$$\frac{(\varphi_1 - \varphi)}{(\varphi - \varphi_2)} = \frac{k_5l + k_7l + k_6}{K_1(k_8l + k_9l + k_{10} + k_{11}K_2l + k_{12} + k_{13}K_2lA)} \times \frac{1}{h_o}$$

as shown in Figure 5. The complexity of this ratio can be removed by fixing some limitations and neglecting some less significant rate constants. Here it was assumed that 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. According to the mathematical approximation, it is obvious that  $k_{12}$  is very small as compared to the sum of the other components in the denominator of the said ratio. Therefore,  $k_{12}$  can easily be neglected without changing the value of the ratio. Now, 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 formation of semithionine through the singly protonated triplet state of thionine while in the 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.

It is concluded that the path of the photochemical reaction of thionine mainly consists of four steps, *i.e.*:

- (1) reaction of protonated triplet excited state of thionine and reductant molecule forming semithionine,
- (2) conversion of protonated triplet excited state of thionine into semithionine by taking hydrogen atom from solvent molecule,
- (3) conversion of protonated triplet excited thionine-reductant complex into semithionine through free radical transfer process, and
- (4) conversion of protonated triplet excited thionine-reductant complex into semithionine through electron transfer process.

These steps are given below:



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



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