Kinetics of Photochemical Reactions of Thionine with Thiourea

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The photochemical reaction of thionine (Th) with an organic reductant such as thioureas was studied in absolute methanol at constant temperature 25±0.1°C. Spectrophotometric methods were adopted for the determination of the values of absorbances in the presence of extremely dissociated, undissociated and partially dissociated acridine in absolute methanol. The acidity of the reaction solution H_0 was controlled by using acetate buffer solutions. The effect of variables like concentration of thiourea, acidity an temperature on quantum yield (ϕ) was studied and the results were interpreted in terms of reaction mechanism. It was found that the quantum yield of the reactions of thionine with thiourea is controlled by two equilibria between (i) triplet state of thionine with proton and protonated triplet state of thionine, and (ii) protonated triplet state of thionine with reductant and associated complex ($Th{\cdot}H_{2T}^{++}{\cdot}AH_2$).

Introduction

Investigations of some qualitative and quantitative nature using organic reductants have been reported by several workers.[1−7] Kostryukova et al.[8] observed the quantum yield of about 10^{-4} for thionine−urea and thionine−glucose systems, using unfiltered light beam form a 1000-watt projector lamp. The temperature coefficient of the reaction was found to be 1.2. The authors assumed that only the region of light absorbed by thionine in the visible spectrum is responsible for the photochemical reaction. Photoreduction of thionine and methylene blue in aqueous solutions were studies by Guler et al.[9−10] and Getoff et al.[11−13] Thionine has been frequently used as a sensitizer of the photochemical reaction.[14] Kraemer er al.[15] reported that photooxygenation of allylthiourea, with thionine as sensitizer takes place via radicals at high allylthiourea concentration. Most of the earlier work was of qualitative nature and attention was not paid to the kinetics of the processes.

The aim of the present work is to study the influence of concentration of thiourea, acidity and temperature on quantum yields of the photochemical reduction of thionine using absolute methanol as non-aqueous medium and to interpret the results in terms of reaction mechanism.

Results and Discussion

The acidity of the reaction solution was measured by Hammett acidity function as $H_0 = -\log h_0$, and

$$h_0 = [H^+]f_{H^+} \cdot f_B/f_{BH^+} \quad (1)$$

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^+. An optical method described earlier[16,17] using acridine as base indicator was used in order to determine acidity of the solution (H_0).

The intensity of light (I_0) was determined with a photoemission cell connected in series with an ammeter, using the following expression:

$$I_0 = (x/20)(0.00147/2.066 \cdot 10^5)\ \text{Einstein/s} \quad (2)$$

where x is the difference between the current recorded on the ammeter before striking the photocell and after exposing the light.

The quantum yield of the reactions of thionine with thiourea (ϕ) were calculated using the following relation:

$$\log \frac{(D_m - D_{nt})}{D_{nt}} = \frac{I_0(1-\alpha)\phi\varepsilon LT}{2.303\ V} + \log \frac{(D_m - D_{ni})}{D_{ni}} \quad (3)$$

The plot between $\log \frac{D_m - D_{nt}}{D_{nt}}$ and time 't' was a straight line. The molar extinction coefficient ε for thionine in absolute methanol at 605 nm was taken as $8.46 \cdot 10^4 \cdot dm^3 \cdot mol^{-1}\ cm^{-1} \cdot L$, the length of the path travelled by the beam in the cell was 7.0 cm. I_0, and α, the fraction of the light lost at each windows of the reaction cell were measured during the experiments, V, the volume of the solution was observed as 0.0325 dm^3.

$$\phi = 5.488 \cdot 10^{-4} \times \text{slope}/I_0(1-\alpha) \quad (4)$$

Thionine with various concentrations of thiourea in buffered methanolic solutions at two different values of acidity were irradiated. The quantum yield was determined at a fixed concentration of thionine at different thiourea concentrations. The results are summarized in Table 1.

Table 1 and Figure 1 represent that a fixed value of acidity H_0, the value of quantum yield increases with the rise in the concentration of thiourea. The plots of the reciprocal of the quantum yield (1/ϕ) against the reciprocal of the concentration of thiourea [$1/AH_2$] at two different acidities (5.80 and 6.09, respectively) shown in Figure 1 are straight lines. These plots have positive intercepts. On extrapolation of the straight lines, the intercept on y-axid gives the limiting value of quantum yield for infinite concentration of

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Table 1. Influence of thiourea concentration of the quantum yield (ϕ) of the reaction

[Thionine]: $6.0 \cdot 10^{-6}$ mol · dm^{-3} Buffer: Acetate
Solvent: Absolute methanol Temperature: 25 ± 0.1 °C

10^4 [AH$_2$] (mol dm^{-3})	$10^{10} \cdot I_0$ (Einst/s)	ϕ	10^{-3}/[AH$_2$] (dm^{-3} mol)	1/ϕ
H_0 (average): 5.80				
4.61	2.99	0.046	2.17	21.74
6.15	3.03	0.055	1.63	18.18
7.38	2.91	0.064	1.35	15.62
9.23	2.91	0.080	1.08	12.50
36.90	2.91	0.128	0.27	7.81
55.40	2.76	0.151	0.18	6,62
H_0 (average): 6.09				
5.54	2.91	0.037	1.80	27.02
7.38	2.82	0.045	1.35	22.22
11.10	2.91	0.056	0.90	17.85
27.70	2.87	0.076	0.36	13.15
44.30	2.91	0.087	0.22	11.49
88.60	2.95	0.097	0.11	10.31

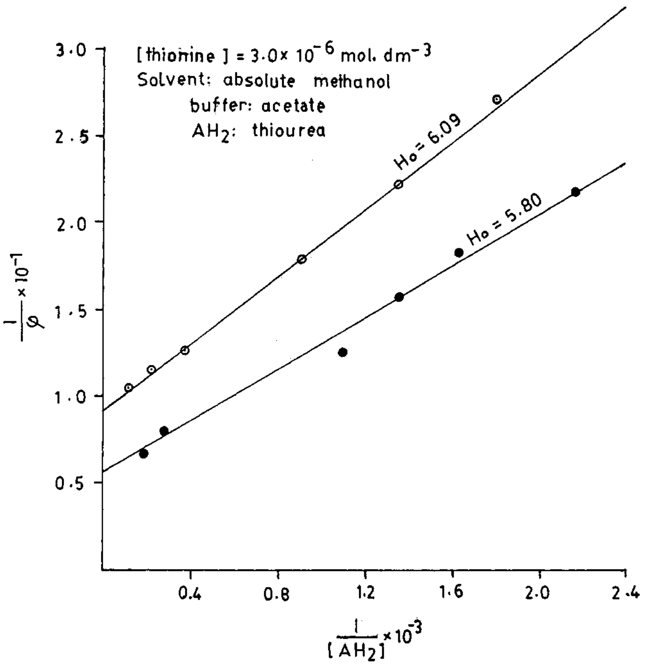

Figure 1. Plot of 1/ϕ against 1/[AH$_2$]

thiourea. The values of ϕ for infinite concentration of thiourea. at H_0 5.80 and 6.09 are 0.188 and 0.108, respectively.

The effect of variation of acitity was studied at a fixed concentration of thionine of $3.0 \cdot 10^{-6}$ mol · dm^{-3} in buffered solutions. The concentration of thiourea in absolute methanol was also kept constant. The results of the measurements of quantum yield data are present in Table 2. When the quantum yield was plotted against H_0, the curve as shown in Figure 2 was obtained. It is evident that the quantum yield increases in the region H_0 6.48−5.58. At higher values of acidity, the magnitude of the quantum yield is more of less constant. The plot of 1/ϕ against $1/h_0$ is a straight line as shown in Figure 3. Figure 4 shows that the plot of $(\phi_1 - \phi)/(\phi - \phi_2)$ against the reciprocal of $h_0(1/h_0)$ is a straight line passing through the origin. Here ϕ_1 and ϕ_2 are the quantum yields at extreme acidic and basic values, respectively.

The shape of the plot of ϕ against H_0 shown in Figure 2 leads to the conclusion that the quantum yield may be controlled by two excited species of thionine. It is assumed that the triplet state must be initially formed as $Th \cdot H_T^+$. If the effect of H_0 on the triplet state is the result of competition between $Th \cdot H_T^+ + H^+ \rightarrow Th \cdot H_{2T}^{++}$ and $Th \cdot H_T^+ + AH_2 \rightarrow$ products, an increase in acidity will cause a decrease in quantum yield. This is similar to the observed behaviour. It is also assumed that $Th \cdot H_{2T}^{++}$ is associated with AH$_2$ and the following equilibrium is established:

$$Th \cdot H_{2T}^{++} + AH_2 \rightleftharpoons Th \cdot H_{2T}^{++} \cdot AH_2$$

The straight line plots of (1/ϕ) against [1/AH$_2$] shown in Figure 1, indicate that both the intercepts and slopes are the functions of acidity. The intercepts provide limiting values of ϕ for an infinite concentration of thiourea at two different values of acidity.

$$Th \cdot H^+ + h\nu \rightarrow Th \cdot H_S^+;\ \text{rate} = [I_a] \tag{5}$$

where I_a is the conversion from the ground state to the singlet state. On absorption of light, the cation of thionine excited to a singlet state $Th \cdot H_S^+$, from which it returns to the ground state by emitting fluorescence.

$$Th \cdot H_S^+ \xrightarrow{k_1} Th \cdot H^+ + h\nu_f;\ \text{rate} = (1-a)[I_a] \tag{6}$$

Pestemer[18] suggested that fluorescence of thionine is not quenched when photochemical reaction with the substance takes place. Therefore, it can be assumed that the reacting excited state is the triplet state. Hence the reaction:

$$Th \cdot H_S^+ \xrightarrow{k_2} Th \cdot H_T^+;\ \text{rate} = [I_a] \tag{7}$$

must be included.

In the singlet state the excited thionine may be deactivated to the cation Th · H$^+$, by collision with unexcited thionine or with reductant:

$$Th \cdot H_S^+ + Th \cdot H^+ \xrightarrow{k_3} Th \cdot H^+ + Th \cdot H^+ \tag{8}$$

$$Th \cdot H_S^+ + AH_2 \xrightarrow{k_4} Th \cdot H^+ + AH_2 \tag{9}$$

It is proposed that the dye in the triplet state quickly associates with a hydrogen ion, and establishes the equilibrium:

$$Th \cdot H_T^+ + H^+ \rightleftharpoons Th \cdot H_{2T}^{++} \tag{10}$$

$$\mathbf{K_1} = \frac{[Th \cdot H_{2T}^{++}]}{[Th \cdot H_T^+][H^+]} \tag{11}$$

In the triplet state the excited thionine may be deactivated to the cation Th · H$^+$, by collision with reductant molecule:

$$Th \cdot H_T^+ + AH_2 \xrightarrow{k_5} Th \cdot H^+ + AH_2 \tag{12}$$

The triplet state is supposed to react with reductant forming semithionine:

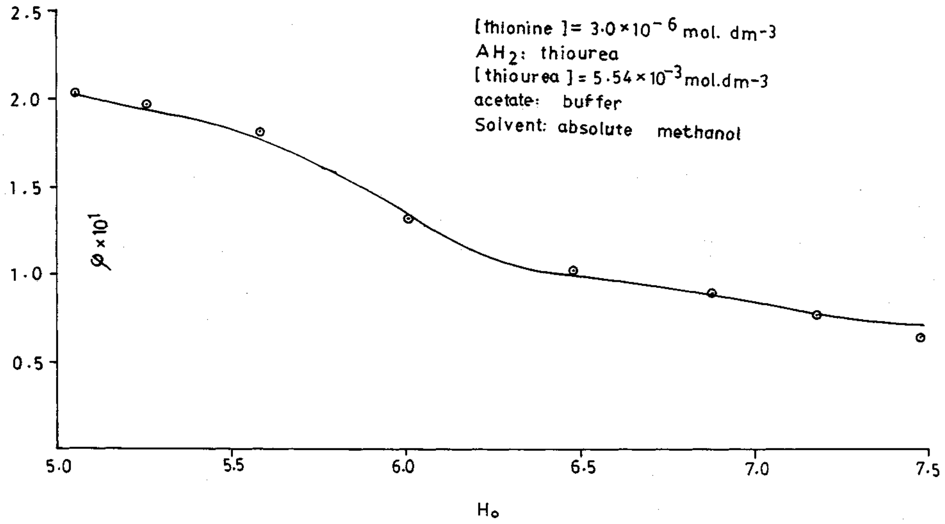

Figure 2. Plot of φ versus H_0

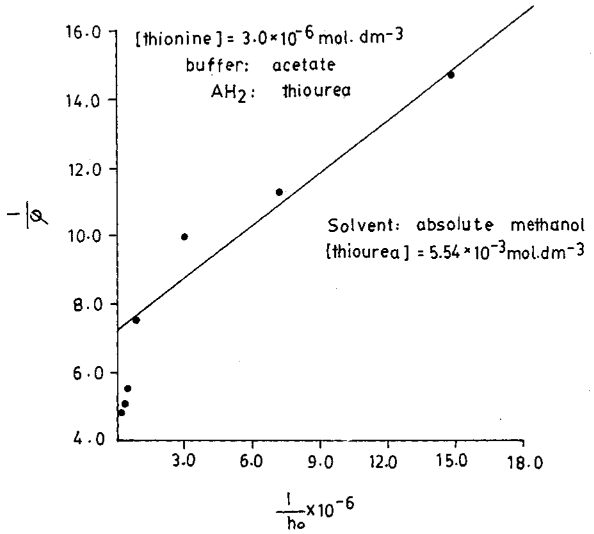

Figure 3. Plot of 1/φ against $1/h_0$

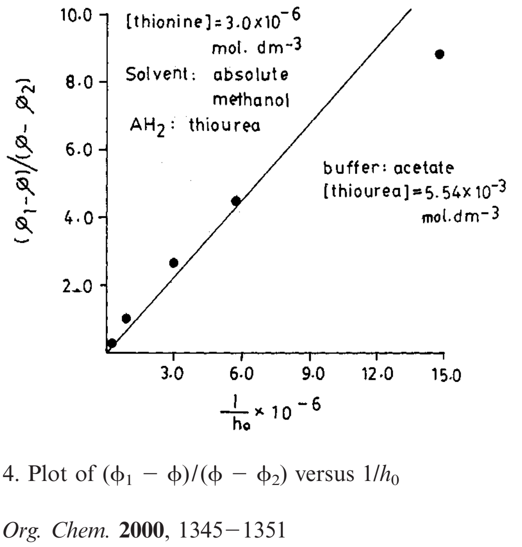

Figure 4. Plot of $(\phi_1 - \phi)/(\phi - \phi_2)$ versus $1/h_0$

Table 2. Acidity − quantum yield measurements

[Thionine]: $3.0 \cdot 10^{-6}$ mol · dm^{-3}	Buffer: Acetate
Solvent: Absolute methanol	AH$_2$: Thiourea
[AH$_2$]· $5.54 \cdot 10^{-3}$ mol · dm^{-3}	Temperature: 25 ± 0.1 °C

H_0	10^{10} I_0 (Einst/s)	φ	1/φ	$\left(\frac{1}{10^6\,h_0}\right)$
5.05	2.95	0.203	4.93	0.112
5.25	2.76	0.196	5.10	0.178
5.58	2.91	0.180	5.55	0.380
6.00	2.83	0.131	7.63	1.000
6.48	2.87	0.100	10.00	3.020
6.86	2.83	0.088	11.36	7.244
7.17	2.99	0.075	13.33	14.791
7.47	2.95	0.062	16.13	29.510

$$\mathrm{Th \cdot H_T^+ + AH_2 \xrightarrow{k_6} Th \cdot H_2^+ + AH} \qquad (13)$$

In the triplet state the excited thionine may from cation Th · H$^+$ by intersystem crossing:

$$\mathrm{Th \cdot H_T^+ \xrightarrow{k_7} Th \cdot H^+} \qquad (14)$$

The protonated triplet species are supposed to react with the reductant forming semithionine which on disproportionation produces the leucothionine:

$$\mathrm{Th \cdot H_{2T}^{++} + AH_2 \xrightarrow{k_8} Th \cdot H_2^{++} + AH_2} \qquad (15)$$

$$\mathrm{Th \cdot H_{2T}^{++} + AH_2 \xrightarrow{k_9} Th \cdot H_3^{++} + AH} \qquad (16)$$

$$\mathrm{Th \cdot H_{2T}^{++} \xrightarrow{k_{10}} Th \cdot H_2^{++}} \qquad (17)$$

Assuming that the Th · H$_{2T}^{++}$ is associated with AH$_2$, the following equilibrium is established:

$$\mathrm{Th \cdot H_{2T}^{++} + AH_2 \rightleftharpoons Th \cdot H_{2T}^{++} \cdot AH_2} \qquad (18)$$

$$\mathbf{K_2} = \frac{[\mathrm{Th \cdot H_{2T}^{++} \cdot AH_2}]}{[\mathrm{Th \cdot H_{2T}^{++}}][\mathrm{AH_2}]} \qquad (19)$$

Reaction with solvent (SH) is:

$$\mathrm{Th \cdot H_{2T}^{++} + SH \xrightarrow{k_{11}} Th \cdot H_3^{++} + S} \qquad (20)$$

By means of internal conversion, the complex looses its energy and subsequently dissociates:

$$\mathrm{Th \cdot H_{2T}^{++} \cdot AH_2 \xrightarrow{k_{12}} Th \cdot H^+ + H^+ + AH_2} \qquad (21)$$

In the presence of unexcited thionine, the oxidation−reduction reaction occurs between the two parts of the complex apparently:

$$\mathrm{Th \cdot H_{2T}^{++} \cdot AH_2 + Th \cdot H^+ \xrightarrow{k_{13}} Th \cdot H_3^{++} + AH + Th \cdot H^+} \qquad (22)$$

where AH is a free radical from $\mathrm{AH_2}$ and $\mathrm{Th \cdot H_3^{++}}$ is semithioine. This is a hydrogen transfer reaction.

By the transfer of the electron, the oxidation−reduction can also take place:

$$\mathrm{Th \cdot H_{2T}^{++} \cdot AH_2 + Th \cdot H^+ \xrightarrow{k_{14}} \underset{\text{(Semithionine)}}{Th \cdot H_2^+} + AH_2^+ + Th \cdot H^+} \qquad (23)$$

$$\mathrm{Th \cdot H_2^+ + H^+ \rightleftharpoons Th \cdot H_3^{++}}\ \text{(Semithionine)} \qquad (24)$$

$\mathrm{Th \cdot H_3^{++}}$ disproportionates to give leucothionine $\mathrm{Th \cdot H_4^{++}}$, and thionine cation $\mathrm{Th \cdot H^+}$:

$$\mathrm{2\,Th \cdot H_3^{++} \xrightarrow{k_{15}} Th \cdot H_4^{++} + H^+ + Th \cdot H^+} \qquad (25)$$

The reactions of the free radical AH cannot be exactly specified but may be written as:

$$\mathrm{2\,AH \longrightarrow Products} \qquad (26)$$

where k_1 to k_{15} are the rate constants of the respective processes given as below:

k_1 = conversion of the singlet state to the ground state,
k_2 = Internal conversion of the singlet state to the triplet state,
k_3 = quenching of the singlet state with unexcited thionine cation,
k_4 = quenching of the singlet state with reductant,
k_5 = quenching of the singly charged triplet state to the ground state by reductant,
k_6 = reaction of singly charged triplet species with reductant to from semithionine,
k_7 = intersystem crossing of the singly charged triplet state to the ground state,
k_8 = quenching of the doubly charged triplet state with reductant,
k_9 = reaction of doubly charged triplet species with the reductant,
k_{10} = internal conversion of the doubly charged triplet species,
k_{11} = reaction with solvent,
k_{12} = internal conversion and dissociation of the complex,
k_{13} = quenching of the complex with unexcited thionine cation,
k_{14} = quenching of the complex with unexcited thionine cation by tansfer of electron,
k_{15} = disproportionation of semithionine to leucotchinone.

Let $[\mathrm{Th \cdot H_T^+}] = a$; $[\mathrm{Th \cdot H_{2T}^{++}}] = b$; $[\mathrm{Th \cdot H_{2T}^{++} \cdot AH_2}] = c$;

$$[\mathrm{Th \cdot H^+}] = A;\ [\mathrm{AH_2}] = l;\ [\mathrm{H^+}] = h_0; \qquad (27)$$

then $\alpha[I_a] = a(k_5 l + k_6 l + k_7)$

$$+ b(k_8 l + k_9 l + k_{10} + k_{11}) + c(k_{12} + k_{13} A)\,.$$

$$\text{Since } \phi = -\frac{\mathrm{d}[\mathrm{Th \cdot H^+}]/\mathrm{d}t}{[I_a]} \qquad (28)$$

from equation (11) and (19)

$$\phi = \frac{(k_6 l + k_0 h_0 l \mathbf{K_1} + k_{11}\mathbf{K_1} h_0 + k_{13}\mathbf{K_1}\mathbf{K_2} h_0 l A)}{2(k_5 l + k_6 l + k_7) + \mathbf{K_1} h_0 (k_8 l + k_9 l + k_{10} + k_{11} + k_{12}\mathbf{K_2} l + k_{13} A \mathbf{K_2} l)} \qquad (29)$$

Let $\phi = \phi_1$ at high h_0, and $\phi = \phi_2$ at low h_0.

At high h_0, a is negligible, b and c are the controlling terms, therefore,

$$\phi_1 = \frac{\alpha(k_9 l + k_{11} + k_{13}\mathbf{K_2} l A)}{2(k_8 l + k_9 l + k_{10} + k_{11} + k_{12}\mathbf{K_2} l + k_{13} A \mathbf{K_2} l)} \cdots \qquad (30)$$

at low h_0, the terms b and c are negligible:

$$\phi_2 = \frac{\alpha(k_6 l)}{2(k_5 l + k_6 l + k_7)} \qquad (31)$$

from equation (29),

$$\frac{(\phi_1 - \phi)}{(\phi - \phi_2)} = \frac{\phi_1}{\phi_2}\ \frac{k_6 l}{(k_9 l + k_{11} + k_{13}\mathbf{K_2} A l)\mathbf{K_1} h_0} \qquad (32)$$

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

From equation (29), if $\phi_2 = 0$, i.e. $k_6 = 0$, therefore,

$$\frac{1}{\phi} = \frac{2}{\alpha} + \frac{2(k_8 l + k_{10} + \mathbf{K_2} k_{12} l)}{\alpha(k_9 l + k_{11} + k_{13} A \mathbf{K_2} l)} + \frac{2(k_5 l + k_7)}{\alpha(k_9 l + k_{11} + k_{13} A \mathbf{K_2} l) h_0 \mathbf{K_1}} \qquad (33)$$

In $\frac{1}{\phi}$ against $\frac{1}{l}$ plots, k_{11} can be neglected towards high l and therefore, equation (33) could be written as:

$$\frac{1}{\phi} = \frac{2(k_5 l + k_6 l + k_7) + h_0 \mathbf{K_1}(k_8 l + k_9 l + k_{10}) + \mathbf{K_2} h_0 \mathbf{K_1} l)}{\alpha(k_6 l + k_9 l h_0 \mathbf{K_1} + k_{13} h_0 \mathbf{K_1}\mathbf{K_2} A l)} \qquad (34)$$

Thus the intercept of $\frac{1}{\phi}$ against $\frac{1}{l}$ is

$$\frac{1}{\phi_\infty} = \frac{2}{\alpha}\ \frac{(k_5 + k_6 + k_8 h_0 \mathbf{K_1} + k_9 h_0 \mathbf{K_1}) + (k_{12} + k_{13} A)\mathbf{K_2} h_0 \mathbf{K_1}}{(k_6 + k_9 h_0 \mathbf{K_1} + k_{13} h_0 \mathbf{K_1}\mathbf{K_2} A)} \qquad (35)$$

and the slope is:

$$\frac{1}{\alpha} = \frac{(k_1 + k_{10} h_0 \mathbf{K_1})}{(k_6 + k_9 h_0 \mathbf{K_1} + k_{13} h_0 \mathbf{K_1}\mathbf{K_2} A)} \qquad (36)$$

At infinite concentration of the reductant, the intercept $\frac{1}{\phi_\infty}$ gives the limiting quantum yield.

Thus the plot of $\frac{1}{\phi}$ against $\frac{1}{l}$ can also be written as:

$$\frac{1}{\phi_\infty} = \frac{1}{\phi} + \frac{2}{\alpha}\,\frac{(k_7 + k_{10}h_0\mathbf{K_1})}{(k_6 + k_9h_0\mathbf{K_1} + k_{13}h_0\mathbf{K_1}\mathbf{K_2}A)}\,\frac{1}{l}\,. \tag{37}$$

The values of the intercepts and slopes of the plots of reciprocal of the quantum yield $\frac{1}{\phi}$ against the reciprocal of reductant concentration [1/AH$_2$] as shown in Figure 4 were calculated. These values are also tabulated in Table 3.

Table 3. Calculated intercepts[a] and slopes[a] of the plots $\frac{1}{\phi}$ vs. [1/AH$_2$] (solvent: absolute methanol)

Thiourea	H_0	Intercept	10^3 slope (mol · dm^{-3})
	5.80	5.31 ± 0.46	7.51 ± 1.74
	6.09	9.34 ± 0.16	9.70 ± 0.83

[a] Figure errors determined by computation are shown above.

The ratios of the rate constants were calculated using the different equations of the general mechanism.

For instance, the ratios $\frac{2}{\alpha}\,\frac{(k_5 + k_6)}{k_6}$, and $\frac{2}{\alpha}\,\frac{(k_8 + k_9)}{(k_9 + k_{13}\mathbf{K_2}A)}$ were calculated from $\phi_2 = \frac{\alpha k_6 l}{2(k_5 l + k_6 l)}$ (k_7 is neglected), and $\phi_1 = \frac{(k_9 l + k_{13}\mathbf{K_2}Al)}{2(k_8 l + k_9 l)}$ (k_{10}–k_{13} in the denominator are neglected) respectively. Using the slopes of the plots of $\frac{1}{\phi}$ against [1/AH$_2$], i.e. $\frac{1}{l}$, the ratios of the rate constants $\frac{2}{\alpha}\,\frac{k_7}{k_6}$ and $\frac{2}{\alpha}\,\frac{k_{10}}{(k_9 + k_{13}\mathbf{K_2}A)}$ were calculated. The ratios of the rate constants $\frac{k_6}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}$ were calculated from the plots of $\frac{(\phi_1 - \phi)}{(\phi - \phi_2)}$ against $\frac{1}{h_0}$. The value $\frac{2}{\alpha}\,\frac{(k_{12} + k_{13}A)\mathbf{K_2}}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}$ was determined from the intercept of the plot of $\frac{1}{\phi}$ against [1/AH$_2$] i.e. $\frac{1}{l}$. The values of the ratios of the rate constants for the reactions of thionine with thiourea in absolute methanol are summarized in Table 4.

$\frac{2}{\alpha}\,\frac{(k_5 + k_6)}{k_6}$ is concerned with the $\mathrm{Th}\cdot\mathrm{H}_\mathrm{T}^{+}$ species. At the comparative high acidity region the quantum yield is due to k_6. The rate constant k_6 as compared to k_5 is low with thiourea in absolute methanol.

k_8 and k_9 are due to $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ in the comparatively low acidity region. The rate constants k_8 and k_9 are responsible to advance the chemical reaction. $(k_9 + k_{13}\mathbf{K_2}A)$ is exceptionally more in absolute methanol with *N*-phenylglycine[16] than thiourea as the reductant. This is either due to high reactivity of the reductant or due to the side reaction of the products. The value of $(k_8 + k_9)/(k_9 + k_{13}\mathbf{K_2}A)$ for thiourea indicates that the reaction is also followed by association. Thiourea may be associated more with the protonated triplet state of thionine, as compared to *N*-phenylglycine.

Table 4. Ratios of the rate constant[a]

	Reductant (thiourea)
$\frac{2}{\alpha}\,\frac{(k_5 + k_6)}{k_6}$	16.13
$\frac{2}{\alpha}\,\frac{(k_8 + k_9)}{(k_9 + k_{13}\mathbf{K_2}A)}$	4.93
$\frac{k_6}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}\,10^5$	1.96 ± 0.50
$\frac{2}{\alpha}\,\frac{k_{10}}{(k_9 + k_{13}\mathbf{K_2}A)}\,10^3$	7.57 ± 1.74
$\frac{2}{\alpha}\,\frac{k_5}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}\,10^3$	0.31 ± 0.08
$\frac{2}{\alpha}\,\frac{k_7}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}\,10^8$	19.5 ± 6.0
$\frac{2}{\alpha}\,\frac{k_7}{k_6}\,10^3$	9.70 ± 0.83
$\frac{2}{\alpha}\,\frac{(k_{12} + k_{13}A)\mathbf{K_2}}{(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}}$	0.85 ± 0.00
$\frac{\alpha}{2}\,\frac{k_6}{(k_{10}\mathbf{K_1})}\,10^2$	0.26 ± 0.01

[a] Figure errors determined by computation are shown above.

$k_6/(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}$ is the ratio of the rate constant responsible for producing products by their species i.e. triplet state of thionine, protonated triplet state of thionine and association of protonated triplet state of thionine with reductant.

$(2k_7/\alpha k_6)$ is the ratio of the rate constant between intersystem crossing rate and the products forming rate for species $\mathrm{Th}\cdot\mathrm{H}_\mathrm{T}^{+}$ $2k_{10}/\alpha(k_9 + k_{13}\mathbf{K_2}A)$ is the ratio of the rate constant between internal conversion rate of $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ and the products forming rate due to the species $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ and $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}\cdot\mathrm{AH}_2$.

$(\alpha k_6/2k_{10}\mathbf{K_1})$ is the ratio of the rate constant responsible for producing products by the species $\mathrm{Th}\cdot\mathrm{H}_\mathrm{T}^{+}$ and internal conversion process of $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ $2k_7/\alpha(k_9 + k_{13}\mathbf{K_2}A)\mathbf{k_1}$ is the ratio of the rate constant between intersystem crossing of the process $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ and the rate of formation of the products by $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}$ and association.

k_{12} and k_{13} are due to the dissociation of the complex $\mathrm{Th}\cdot\mathrm{H}_{2\mathrm{T}}^{++}\cdot\mathrm{AH}_2$ and the products forming by the thionine cation with association. k_9 is due to the combination of thiourea with the protonated triplet state of thionine. The ratio $2(k_{12} + k_{13}A)\mathbf{K_2}/\alpha(k_9 + k_{13}\mathbf{K_2}A)\mathbf{K_1}$ indicates that the mechanism of the reactions of the thionine with thiourea also involves the association. Various equations were derived from the postulated mechanism. These equations show the relations between $1/\phi$ versus $1/[\mathrm{AH}_2]$, $1/\phi$ versus $1/h_0$, and $(\phi_1 - \phi/\phi - \phi_2)$ versus $1/h_0$. The plots of $1/\phi$ versus $1/[\mathrm{AH}_2]$, $1/\phi$ versus $1/h_0$, and $(\phi_1 - \phi/\phi - \phi_2)$ versus $1/h_0$

drawn from experimental data lead to the conclusion that there exists linear relations, which is in accordance with the equations derived from the proposed mechanism.

The effect of the variation of temperature on quantum yield was studied at fixed concentrations of thionine and thiourea. The acidity of the reaction solution was maintained constant. The results are summarized in Table 5. Results show that an increase in temperature increases quantum yield. The average value of temperature coefficient for a rise of temperature of five degree is 1.264.

Table 5. Effect of temperature on quantum yield

Thionine: $3.0 \cdot 10^{-6}$ mol · dm^{-3} Buffer: Acetate
Solvent: Absolute methanol AH_2: Thiourea
$[AH_2]$: $3.69 \cdot 10^{-3}$ mol · dm^{-3}

	Temperature, °C				
	25	**30**	**35**	**40**	**45**
ϕ	0.128	0.168	0.186	0.251	0.325
Temperature coefficients					
ϕ_{30}/ϕ_{25}	ϕ_{35}/ϕ_{30}	ϕ_{40}/ϕ_{35}	ϕ_{45}/ϕ_{40}		
1.31	1.11	1.35	1.29		

The temperature coefficient was found to be about 1.2 for thionine thiourea and thionine-glucose systems reported earlier by Kostryukova[8]. Sawkar[19] also reported the temperature coefficient as 1.3 for thionine with allylthuourea. These results are in agreement with those of the present work. Weber[20] also found the influence of temperature on the reactions of thionine with allylthiourea and diethylallylthiourea. He postulated that the number of effective collisions of the excited thionine with the reductants increases with the rise in temperature. A temperature coefficient of 1.61 was observed with 0.01% diethylallylthiourea. However, as the concentration of diethylallylthiourea was increased to 1.00%, the temperature coefficient decreased to 1.03.

The association constant of the most of the bases decreases as the temperature is increased. The values of the association constants $\mathbf{K_1}$ and $\mathbf{K_2}$ could be assumed to decrease with the rise in the temperature

However, the quantum yield of the reactions of thionine with thiourea was found to increase with the increase in temperature. It seems, therefore, that the reaction:

$$Th \cdot H_{2T}^{++} \cdot AH_2 + Th \cdot H^+ \xrightarrow{k_{13}} Th \cdot H_3^{++} + AH + Th \cdot H^+$$

requires some activation energy.

Conclusions

The quantum yield of the reactions of thionine with thiourea is controlled by two equilibria between (i) triplet state of thionine with proton and protonated triplet state of thionine, (ii) protonated triplet state of thionine with thiourea and associated complex ($Th \cdot H_{2T}^{++} \cdot AH_2$). The quenching of the complex with unexcited thionine cation requires some activation energy.

Experimental Section

All the chemicals such as thionine (oxidation reduction indicator), thiourea, hydrochloric acid, sodium hydroxide, oxalic acid, sodium acetate used were of E. Merck. Extra pure methanol of E. Merck was used after redistillation. Acridine, fluorescent indicator of B. P. H. was used. Nitrogen gas (99.98%) manufactured by Pakistan Oxygen Ltd. was used. The Feiser method[21] was adopted to remove the traces of oxygen from nitrogen. The stock solutions of thionine were preserved in well-stoppered polyethene bottles as suggested by Sawkar.[19]

An apparatus for irradiation of deoxygenated reaction solutions with monochromatic light was designed. Figure 5 shows the general diagram of the optical bench. A high pressure Mazda ME/D box type lamp was used as the light source. The light from the arc was focused by a combination of two convex lenses L_1 and L_2 on to a small hole (∅ 2 mm) in a metal plate. This helps to cut off the stray light and only light from the centres of arc. Lense L_3 was placed at is focal length from the hole of the metal plate O, to obtain a parallel beam of light. Monochromatic yellow light was obtained by passing the beam further through a combination of filter solutions held in 2 compartments cell (F_1 and F_2). Filters used were the combination[22] consisting of 10 ml (100 g $CuCl_2 \cdot 2H_2O$ in 1 l of water) and 90 ml (333 g anhydrous salt in 1 l of H_2O, i.e. 3 mol · dm^{-3}), 1 cm, in the first compartment (F_1) and saturated potassium dichromate solution, 1 cm, in the second compartment of the filter cell (F_2). R denotes the plain reflecting glass which reflected about 10.5% of the filtered light on to a photocell P_2. The light was then passed through the reaction cell (C). M is a magnetic stirrer. P_1 and P_2 represent the photocell used to follow the reaction and to monitor the galvanameters used to indicate the responses of the photocells P_1 and P_2, respectively. The percent transmission and resultant transmission of the filter solutions are shown in Figure 6. The resultant transmission curve shows that about 53% of 579 nm light is transmitted.

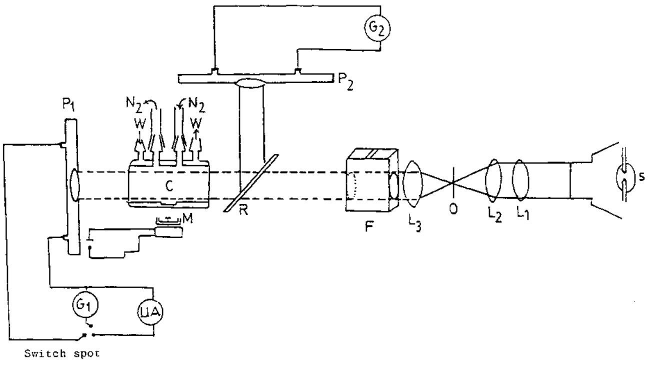

Figure 5. The optical bench

The reaction cell was a modified from of the cell used by Atkins et al.,[22] Sawkar,[19] and Ahmed.[23] In the present work, the arrangement of circulation of water into the reaction cell was made in order to maintain the temperature of the reaction cell constant. A double-walled reaction cell, cylindrical glass tube 7.0-cm in length, 2.5-cm in diameter with flanged ends was constructed as shown in Figure 7. Half way along with lower length of the cell

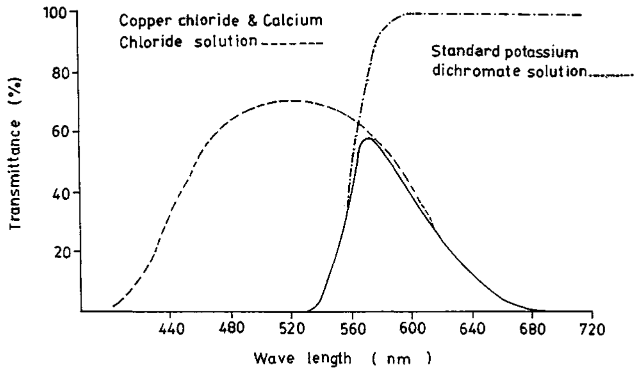

Figure 6. Transmission curves of the filter solutions

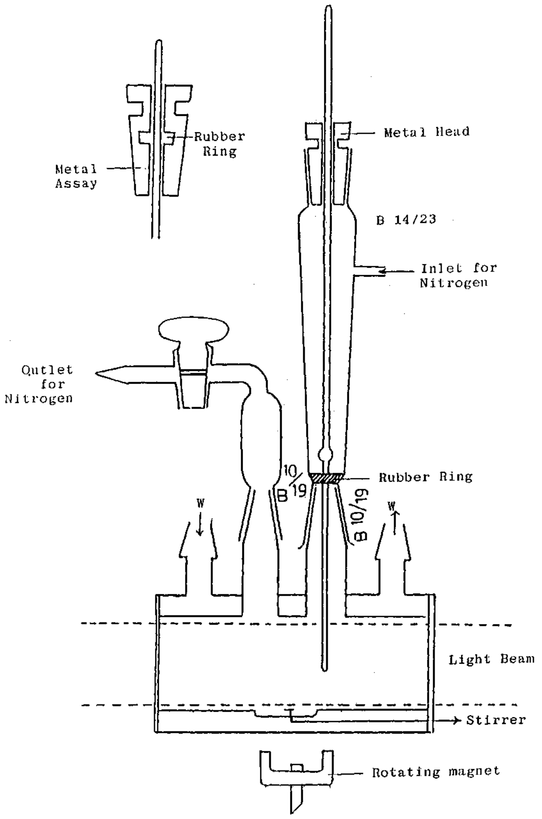

Figure 7. The reaction cell

was made a depression of about 1.5-cm in diameter wherein a steel needle completely sealed in a glass tube was placed which served as a magnetic stirrer. Two B 10 joints were attached to cell at upper length, one for the intake of oxygen free nitrogen through a retractable tube and the other end as an exit with an ordinary tap fitted to it. At the ends of the reaction cell, two joints as shown in Figure 4 were connected to the thermostatic bath (type T-52, manufactured by Haake, Karlsruhe/Germany) for circulation of water in the outer part of the cell.

32.5 ml of reaction mixture containing known volumes of thiourea and buffer solutions in methanol were pipetted out into reaction cell. The mercury lamp was on for 30 minutes before exposing the reaction solution to monochromatic yellow light. In order to make the reaction solution inert, oxygen free nitrogen was bubbled for thirty minutes. The photocell response on galvanometer was noted with no cell in the beam (D_0), with cell containing methanol as solvent (D_m) and with cell containing reaction solution with monochromatic yellow light (D_{ni}).

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