Front. Chem. China 2011, 6(2): 120–126
DOI 10.1007/s11458-011-0235-8

RESEARCH ARTICLE

Thionine sensitized areobic photooxidation of thiourea in acidic medium

Rafia AZMAT (✉) and Nida SALEEM

An investigation of the thionine sensitized aerobic photooxidation of thiourea was observed spectrophotometrically at a wavelength of 598 nm. Articles reported two types of reactions which generally occur in the presence of oxygen: 1) Singlet oxygen, produced by dye sensitization due to the hydrolysis that reacts with thiourea to form oxidative products like urea and other sulfur-containing fragments and 2) bleaching of dye, which leads to the reduction. The rate of reaction in all studied parameters followed first order kinetics with respect to maximum absorption of the dye in the visible band region. Reaction kinetics was significantly dependent upon the medium and the reaction accelerated more rapidly at low pH. A direct relation was exhibited between the thiourea concentration and dye sensitizer, which was not pragmatic with the concentration of dye. The reaction was effected by the temperature, and the values of energy parameters suggested that the energy of activation was low while the entropy of activation increases with the rise in temperature, which indicated a highly solvated state of intermediate complex. Lower value of ΔH^* and ΔG^* at elevated temperature showed that free energy is the driving force for the completion of reaction. A mechanism based on the above findings has been suggested.

Keywords thionine sensitized, photo oxidation, thiourea, singlet oxygen, fragment

1 Introduction

Photosensitized oxidations have been of much interest and of importance to a chemist and a biologist who is commonly involved in killing bacteria in the presence of light and dye sensitizer. Recent studies on simple chemicals have led to rapid advances in the understanding of photosensitized oxidation. Not only one pathway but a number of different pathways have been shown to occur [1,2]. Photosensitized oxidation of amines and other compounds showed that dyes act as a sensitizer in a large number of these reactions [3]. Some reaction reported that in aerobic conditions singlet oxygen is involved in reactions, whereas in others, the interaction of the excited dye with the substrate has been postulated. Vaidya et al. [4] reported that the singlet oxygen participation in the reaction of the dye-sensitized photooxidation of thiourea results in the formation of urea. The reaction pathways between thiourea and substituted thioureas do not undergo photolysis under nitrogen or photo-oxidation under oxygen, even under long exposure to UV light when singlet oxygen produced by dye sensitization reacts with thioureas to form cyanamides, ureas, heterocyclic condensation products and sulfur-containing fragments [5].

Thiourea is a toxic and cancer supporting agent and its derivatives are known as corrosion inhibitors. The reaction of thiourea with hydrogen peroxide under certain conditions produces powerful reductive bleaching agents that are routinely used in textile industry and release high concentration of thiourea in industrial wastes [6]. Epling et al. [7] proposed that, in addition to photocatalytic oxidation mechanism for TiO_2 reactions, evidence for two kinds of electron transfer mechanisms were also observed. They are “photosensitized reduction” and “photosensitized oxidation” in which natural sunlight was effectively used to photo bleach the dye [8–18]. This research work was undertaken to ascertain the role of atmospheric oxygen in dye redox reaction as a reactive intermediate. And a mechanism of both dye reduction and oxidation of reducing agent based on kinetics have been described at optimum parameters in the relevant section of this paper.

2 Experimental

All the chemicals used were of Merck grade and used without further purification [9–11].

Experimental measurements were divided into four parallel sessions, preparation of solutions, kinetics measurements, product analysis and stoichiometry.

2.1 Preparation of solution

All the stock and standard solutions and appropriate dilutions were made in deionized distilled water by dissolving the requisite amounts of reagents. Aqueous solutions of HCl and H_2SO_4 were standardized by titrating against standard Na_2CO_3. Urea was analyzed by a qualitative method.

Received February 21, 2011; accepted March 5, 2011

Department of Chemistry, Jinnah University for Women, Karachi 74600, Pakistan
E-mail: rafiasaeed200@yahoo.com

2.2 Kinetics measurements

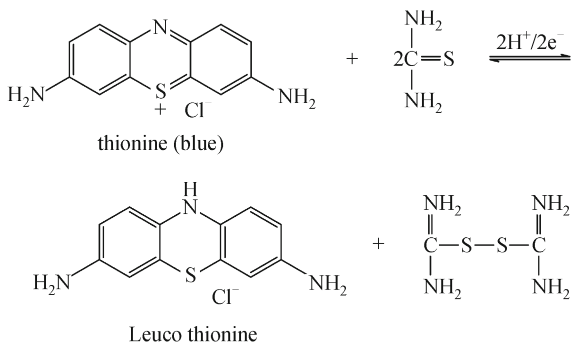
All the kinetics measurements were conducted in a thermostatic reaction vessel in open atmospheric oxygen. Dilutions were made according to the needs of experiments. At various time intervals the samples were removed and the optical density of dye was recorded at 598 nm on UV-visible Schimadzo spectrophometer 180A.

2.3 Product analysis

The reaction mixture was prepared by the method described by Jonnaladadda [8] and analysed using GC-mass spectrophotometer. The chromatograph showed peaks in the region as reported earlier, which showed urea and dithiodiformamidinium [8] with leuco thionine as a main product.

2.4 Stoichiometry

The stoichiometry of the reaction mixture i-e Th and TU were determined by mixing the reagents in molar ratios of 2∶1,1∶1 and 1∶2 with HCl in excess [8]. Immediate de-coloration was observed in the bottle contain molar ratio in 1∶2 as compared to other ratios, which showed that Th reacts with thiourea in 1∶2 ratio. The residual reactant concentration was analyzed and the overall reaction may be proposed according to the following scheme.



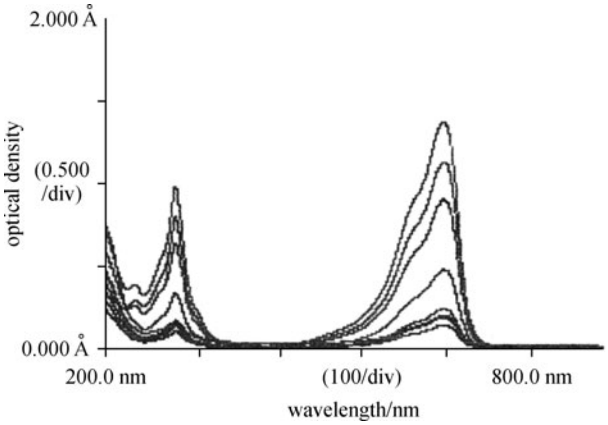


Figure 1 Spectral changes of thionine at different initial concentrations

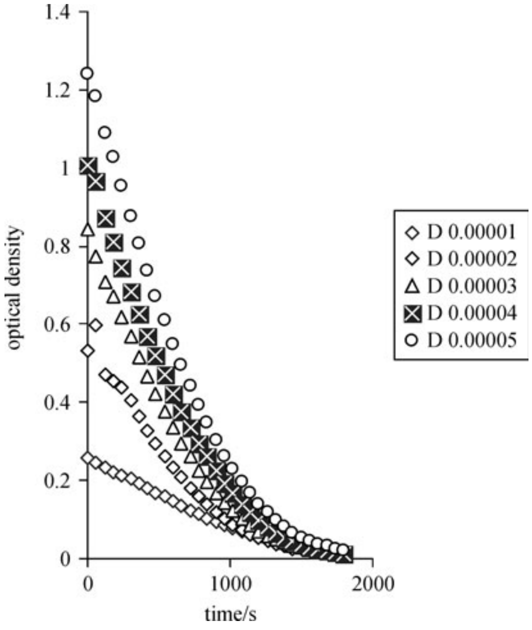


Figure 2 A plot of O.D vs. time at different concentrations of dye for Thionine – thiourea reduction reaction in acidic medium

3 Results and discussion

Spectral changes (Fig. 1) with respect to different initial concentrations of dye were recorded for $\lambda_{\max}$ to study the reaction kinetics and found at 598 nm.

The reaction was monitored by measuring absorbance at 598 nm as the function of time. As shown in Fig. 2, a plot of optical density vs. time is the excellent representation of first order kinetics with respect to thionone concentration in acidic medium. The pseudo first order rate constants were determined from each dye concentration from the slope of line and reported in Table 1. The value of the rate constant k showed that redox reaction is independent of the dye [9–11] concentration while ThH, urea and dithioformamidinium were found to be the main primary products of the reaction. Since thiourea has a lone pair on nitrogen, there exist possibilities of complex formation with thiourea which can influence the reaction. The effect of increasing concentration of the dye was examined, and no effect on the rate constant was observed, which reflects that in the region of essentially complete absorption of incident radiation any increase in the Th concentration ceases to affect the rate (Table 1). This rules out the possibility of any complex formation because if the complex is formed the rate will increase, whereas the rate

Table 1 Redox reaction of thionine and thiourea with different concentrations of dye

Thionine/(10^{-5} mol·dm^{-3})	v/(10^{4} mol·dm^{-3}s^{-1})	k /(10^{3} s^{-1})	1/k/(10^{-3} s)	Decoloration/%
1.00	−1.00	2.30	0.43	94.6
2.00	−3.00	2.30	0.43	94.6
3.00	−5.00	2.30	0.43	94.6
4.00	−5.00	2.30	0.43	94.6
5.00	−5.00	1.70	0.58	92.2

thiourea = 1.0×10^{-1} mol·dm^{-3}; [HCl] = 1.0×10^{-1} mol·dm^{-3}

Table 2 Redox reaction of thionine and thiourea with different concentrations of reductant

Thiourea/(10^{-1}mol·dm^{-3})	v/(10^{4} mol·dm^{-3}s^{-1})	k/(10^{3} s^{-1})	1/k/10^{-3}	Decoloration/%
0.50	1.00	0.40	2.500	50.95
1.00	2.00	1.00	1.000	85.02
1.50	2.00	1.70	0.5882	94.4
2.00	2.00	2.10	0.4761	96.73
2.50	2.00	2.30	0.5263	96.83

thionine = 2.0×10^{-5}; HCl = 1.0×10^{-1} mol·dm^{-3}

decreases with the increase in concentration (Table 1) since the concentration of products should rise at higher concentration of dye. Table 2 showed the results with varied initial concentrations of reductant for constant concentration of dye and acid. The plot of reductant and k gave a linear line with slope equal to 0.98, suggesting first order kinetics with respect to thiourea concentration [9–14]. No further reaction was observed in the absence of light, which showed that dye excitation must be required for initiating dye sensitizing reactions, or negated any ground states complexation with thiourea.

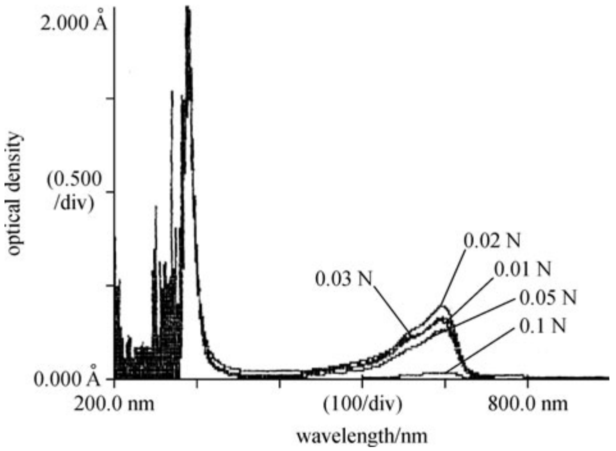


Figure 3 Spectral changes of thionine at different initial concentrations of acid

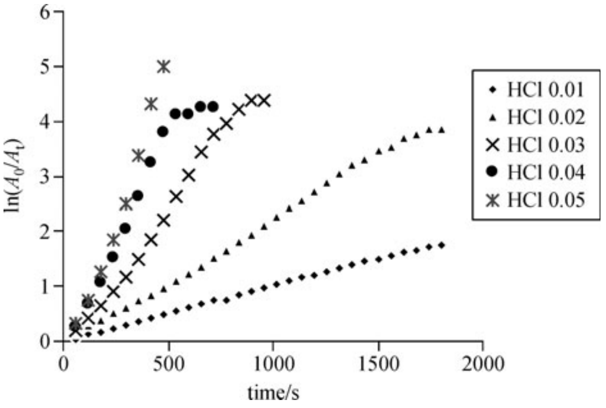


Figure 4 A plot of ln A_O/A_t vs. time for redox reaction of thionine and thiourea

3.1 Effect of H^+ on redox reaction

Effect of increasing concentration of H^+ ions on redox reaction of thionine and thiourea was studied by scanning the spectra under various concentrations of HCl as shown in Fig. 3. And the plots of ln(A_O/A_t) vs. time in Fig. 4 represent the formation of leuco dye without change in wavelength and support the formation of ThH_2^{2+} and ThH_2^{+} and first order kinetics with respect to H^+ concentration respectively. Whereas the decrease in the rate constant (Table 3) with the further increase in concentration of HCl may be involved in secondary reactions. The observed first order kinetics suggested that the rate limiting step involves one molecule of thiourea and one molecule of dye with two molecules of H^+ ions. The combination reaction with the bleaching of dye like urea, and thioformadinium formation as a result of oxidation of thiourea could also be rapid at higher concentration of acid and stabile under acidic condition [6]. The kinetics measurements reported in Table 3 propose a mechanism for the oxidation of thiourea to urea using the reduction of thionine through change in absorbance of dye as a main recorded

Table 3 Effect of acid concentration on redox reaction of thionine

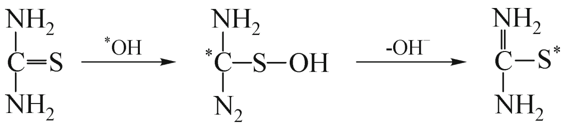
HCl/(10^2 mol·dm^{-3}).	v/(10^3 mol·dm^{-3}s^{-1})	K/(10^2 s^{-1})	1/k/10^{-2}	Decoloration/%
1.00	−0.200	0.100	10.00	−71.7
2.00	−0.200	0.200	4.34	97.98
3.00	−0.400	0.5200	1.92	98.729
4.00	−0.600	0.6800	1.47	98.583
5.00	−0.600	1.14	0.87	99.4
10.0	−1.300	2.06	0.48	99.53
15.0	−1.100	1.36	0.73	98.5
20.0	−2.700	−4.84	−0.20	0.000

thionine = 2.0×10^{-5}; thiourea = 1.5×10^{-1} mol·dm^{-3}

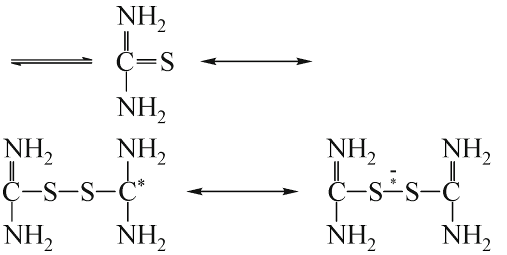
parameter. Being pH dependent, dye reduced to leuco dye with the formation of thiourea radical. It is of interest that dye sensitization processes in some cases involve hydrogen abstraction, and electron transfer process or participation of oxygen (as observed in the present investigation,) generates powerful reducing agent, like in this process in which the oxidation of thiourea leads to urea and dithioformamidinium [15–21].

$$H_2O \xrightarrow[\text{radiation}]{\text{ionization}} e_{aq}^{-}, {}^{*}OH, H^{*}, H^{+}, H_2O_2, H_2 \qquad (1)$$

OH ion produced can attack the carbon sulpher double bound [6]



$$\underset{NH_2}{\overset{NH_2}{C}}{=}S \xrightarrow{{}^{*}OH} {}^{*}\underset{N_2}{\overset{NH_2}{C}}-S-OH \xrightarrow{-OH^{-}} \underset{NH_2}{\overset{NH_2}{C}}-S^{*} \qquad (2)$$

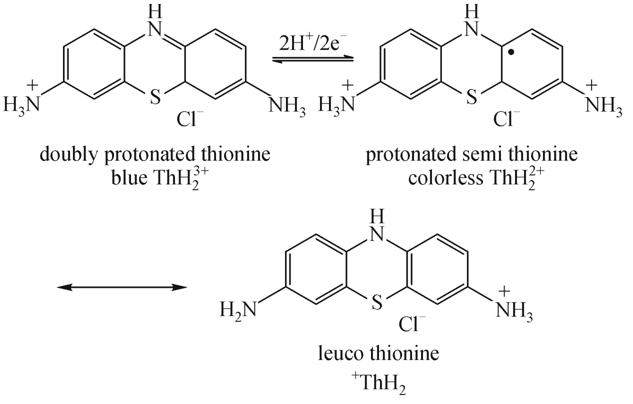


$$\rightleftharpoons \underset{NH_2}{\overset{NH_2}{C}}{=}S \longleftrightarrow$$
$$\underset{NH_2}{\overset{NH_2}{C}}-S-S-\underset{NH_2}{\overset{NH_2}{C}}{}^{*} \longleftrightarrow \underset{NH_2}{\overset{NH_2}{C}}-S\overset{-}{\underset{*}{-}}S-\underset{NH_2}{\overset{NH_2}{C}} \qquad (3)$$

Jonnaladadda & Tshabalala [8] and Vaidya et al. [4] also reputed similar species of thiourea with decoloration of tolidine blue as a oxidation product of thiourea to dithiodiformadinium (Eq. (3))and urea respectively.

3.2 Effect of pH on redox reaction

The reaction rate constants were determined as a function of pH (1.70–12.01) by varying concentration of acid and base and the maximum was found at pH 1.94 (Table 4). This may be due to the protonation of the dye in the studied pH range, which showed that dependence is related with the leuco dye formation. As reported earlier two one electron transfer steps may be for the reduction of Th in acidic solution. At this low pH intermediate the products would exist in protonated form as ThH_2^{2+} and ThH_2^{+} species respectively according to the following pathway.



The decrease in the values of rate constant reported in Table 4 at higher pH may be related to the oxidation of thiourea because OH radical induced oxidation of thiourea in aqueous solution may be attributed to an absorption of radiation, which causes the photolysis of water molecule according to scheme (1), or at high pH more OH radical [16] will be produced which lowered the rate of reaction [Table 4]

Table 4 Effect of pH on redox reaction of thiourea and dye

pH	v/(mol·dm^{-3}s^{-1})	k/s^{-1}	1/k	Decoloration/%
1.70	−0.001	0.0069	144.927	89.1
1.94	−0.0011	0.0119	84.03	89.6
2.12	−0.0011	0.0074	135.135	79.8
2.36	−0.0004	0.005	200	95.4
6.99	−0.0003	0.0003	3333.33	43.0
11.47	−0.000005	0.004	250	44.0
11.59	0.000008	−0.00007	−14285.7	23.0
11.86	−0.00002	0.00007	14285.7	10.5
12.01	0.167	0	0	0

thionine = 2.0×10^{-5}; thiourea = 1.5×10^{-1} mol·dm^{-3}

with the formation of radical cation formation of thiourea [16].

3.3 Effect of ionic strength and temperature

The rate of reaction was studied under the influence of varying concentration of salt KCl [11–18] and the results are reported in Table 5. The results showed that the rate of reaction is directly related with the salt concentration and that the rate determining step involves the reaction between two similar charged species.

The rate of reaction was studied as a function of temperature as shown in Table 6. The plot of ln k vs. $1/T$ (K^{-1}) was linear ($r^2 = 0.9881$) and gave an energy of activation $4.96\ \mathrm{kJ \cdot mol^{-1}}$, suggesting a fast reaction between thiourea and thionine. The positive value of ΔH^* ($\Delta H^* = 2.4\ \mathrm{kJ \cdot mol^{-1}}$) indicated that enthalpy is not the driving force for the formation of complex, and entropy is responsible for the formation of complex, which involves two charged species for the redox of dye. The values of energy parameters suggest that transition complex formed have very high degree of freedom, which reveals that the rate determining state is less disorderly oriented relative to reactants [9–11].

3.4 Reaction pathway for redox reaction of dye and thiourea

The following reaction scheme is for the generation of reactive singlet oxygen and excited dye molecule for the observed redox reaction at different media [10].

$$\mathrm{Th} + h\upsilon \rightarrow \mathrm{Th}_S$$

$$\mathrm{Th}_s \xrightarrow{k_1} \mathrm{Th} + h\upsilon' \ \text{Deactivation}$$

$$\mathrm{Th}_s \xrightarrow{k_2} \mathrm{Th}_T \ \text{Conversion}$$

$$\mathrm{Th}^+ \xrightarrow{k_3} \mathrm{Th} \ \text{Deactivation}$$

$$\mathrm{Th}_T + \mathrm{H}^+ \xrightarrow{k_4} \mathrm{Th}_T\mathrm{H} \qquad (4)$$

In the presence of atmospheric oxygen

$$\mathrm{Th}_T + \mathrm{O}_2 \xrightarrow{h\upsilon} \mathrm{O}^*_{2(s)} \qquad (5)$$

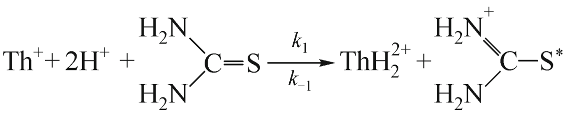
Dye sensitized air oxidation of the thiourea is pH dependent; dye is converted into leuco dye at low pH while at an alkaline pH urea was the primary product according to Eq. (6).

$$\mathrm{O}_2 + \mathrm{NH_2CSNH_2} \xrightarrow{k_5} \mathrm{NH_2CONH_2} \qquad (6)$$

or

$$\mathrm{Th} + \mathrm{NH_2CSNH_2} \rightarrow \mathrm{Th...NH_2SCNH_2} \qquad (7)$$

Rate determining step in the presence of acidic medium involves two protons, one molecule dye and one molecule of reductant, according to Eq. (8)



(8)

Table 5 Effect of salt on redox reaction between thiourea and thionine

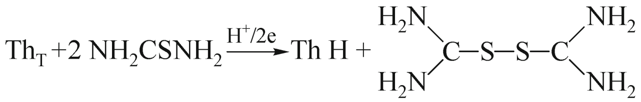
KCl/(mol·dm^{-3})	v/(10^{-4} mol·dm^{-3}s^{-1})	k/(10^{-3} s^{-1})	1/k/10^2	Decoloration/%
0.1	6.0	3.10	3.22	105.07
0.2	6.0	2.00	5.00	106.3
0.3	6.0	4.70	2.12	106.22
0.4	6.0	3.30	3.03	105.68
0.5	6.0	5.70	1.75	102.83

thionine = 2.0×10^{-5}; thiourea = 1.5×10^{-1} mol·dm^{-3}; HCl]= 1.0×10^{-1} mol·dm^{-3}

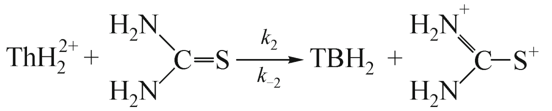
Table 6 Effect of temperature on rate of redox reaction and energy parameters

Temerature	25°C	30°C	35°C	40°C	45°C
v/(mol·dm^{-3}s^{-1})	0.0005	0.0009	0.0011	0.0014	0.0012
k/s^{-1}	0.0101	0.0197	0.0069	0.0404	0.0247
ln k	4.595	3.927	4.976	3.208	3.7009
Decoloration/%	80.1	82.7	87.4	92.9	98.7
E_a/(kJ·mol^{-1})			4.967		
ΔH^*/(kJ·mol^{-1})	−2.4	−2.5	2.5	−2.5	−2.6
ΔS^*/(kJ·mol^{-1})	−63.032	−63.17	−63.30	−63.44	−63.57
ΔG^*/(kJ·mol^{-1})	16.310.931	16.62	16.94	17.25	17.57

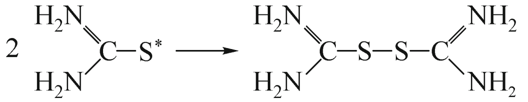
But according to Stoichiometry, two molecules of thiourea are involved in the formation of leuco dye through dithioformamidinium ion with other secondary reactions as follows



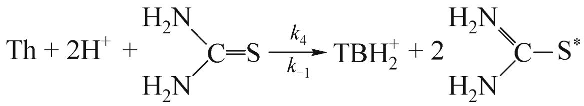
(9)



(10)



(11)



(12)

Finally,

Jonnaladadda & Tshabalala [8] and Liani et al. [22] reported earlier about the same mechanism with simultaneous first and second order involvement of thiourea studying with toludine blue and thiourea and hexacynoferrate (111) respectively.

3.5 Rate law for the redox reaction

The rate law for the redox reaction of dyes usually leads to the photo reduction of excited dye molecules through substrates [12–16]. This usually involves an electron transfer and hydrogen abstraction by reducing the agents in which free radicals are produced in the solution undergoing redox reactions (Eqs. (1–3)). The rate law was determined with respect to dye because the reaction was monitored by recoding the change in optical density of thionine molecule.

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Th}] = v = k_1\left[\mathrm{Th}^+\right]\left[\mathrm{H}^+\right]^2[\mathrm{TU}] \tag{13}$$

At higher concentration of thiourea and acid the rate law was reduced to

$$v = k'\left[\mathrm{Th}^+\right]$$

where

$$k' = k_1\left[\mathrm{H}^+\right]^2[\mathrm{TU}] \tag{14}$$

Considering the higher concentration of thiourea, the order may be changed to the second order with respect to reductant. Therefore the rate of depletion of thionine concentration may be presented as follows

$$v = k_1\left[\mathrm{Th}^+\right]\left[\mathrm{H}^+\right]^2[\mathrm{TU}] + k_4\left[\mathrm{Th}^+\right]\left[\mathrm{H}^+\right]^2[\mathrm{TU}]^2 \tag{15}$$

The rate with respect to thionine

$$v = k'\left[\mathrm{Th}^+\right] \tag{16}$$

where

$$k' = k_1\left[\mathrm{H}^+\right]^2[\mathrm{TU}] + k_4\left[\mathrm{H}^+\right]^2[\mathrm{TU}]^2 \tag{17}$$

or

$$k' = \{k_1 + k_4[\mathrm{TU}]\}[\mathrm{TU}]\left[\mathrm{H}^+\right]^2$$

$$k'' = \frac{k'}{[\mathrm{H}^+]^2} = \{k_1 + k_4[\mathrm{TU}]\}[\mathrm{TU}]$$

$$k'' = \{k_1 + k_4[\mathrm{TU}]\}[\mathrm{TU}]$$

$$\frac{k''}{[\mathrm{TU}]} = k_1 + k_4[\mathrm{TU}] \tag{18}$$

where k_1 and k_4 are the rate constants for the second order dependence of reductant concentration involving both first and second dependence on concentration of thiourea in acidic medium. The plot of ln k vs. thiourea (Fig. 5) showed a linear behavior indicating that the first order reaction is dominant over the second order, whereas the second order may be significant at higher concentrations [8].

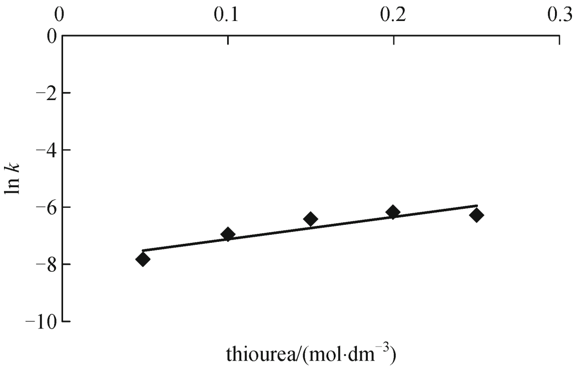


Figure 5 A plot of ln k vs. thiourea concentration for thionine – thiourea reduction reaction in acidic medium

4 Conclusion

It is found that thionine sensitized photoxidation of thiourea gives urea, and dithiodiformadinium as an oxidation product of thiourea, whereas thionine is converted into leuco thionine. Thus it is concluded that thionine sensitized photoxidation of thiourea proceeded through involvement of singlet oxygen as well as dye excited molecule.

References

1. Ram, N.; Sidhu, K. S., *Can. J. Chem*. **1980**, *58*, 2073–2079
2. Azmat, R.; Ahmed, S.; Qureshi, S.; Mohammed, F. V.; Uddin, F., *J App Sci* **2006**, *6*, 2784–2788
3. Ram, N.; Bansal, W. R.; Pandav, B. V.; Sidhu, K. S., *Indian J. Chem*. **1977**, *15B*, 820
4. Vaidya, V. K.; Pitlia, R. L.; Kabra, B. V.; Mali, S. L.; Ameta, S. C., *J Photochem Photobiol A* **1991**, *60*, 47–50
5. Crank, G.; Achmad, M., *J Photochem Photobiol A* **1992**, *64*, 263–271
6. Wang, W.; Schuchmann, M. N.; Schuchmann, H. P.; Knolle, W.; von Sonntag, J.; von Sonntag, C., *J. Am. Chem. Soc*. **1999**, *121*, 238–245
7. Epling, G. A.; Lin, C., *Chemospere* **2002**, *46*, 561–570
8. Jonnalagadda, S. B.; Tshabalala, D., *Int. J. Chem. Kinet*. **1992**, *24*, 999–1007
9. Azmat, R.; Yasmeen, B.; Uddin, F., *Asian J. Chem*. **2007**, *19*, 1115
10. Azmat, R.; Uddin, F., *Canadian J. Pure and Appl. Sci*. **2008**, *2*, 275
11. Azmat, R.; Qamer, N.; Saeed, A.; Uddin, F., *Chin. J. Chem*. **2008**, *26*, 631–634
12. Jonnalagadda, S. B.; Dumba, M., *Int. J. Chem. Kinet*. **1993**, *25*, 745–753
13. Uddin, F.; Hasnain, Q. Z., *Kuwait J. Sci. Engg*. **2002**, *29*, 67
14. Uddin, F., *Eur. J. Org. Chem*. **2002**, *7*, 1345
15. Sharma, V. K.; Vishwas, N. J.; Millero, F. J.; O'Connor, D.; Rivera, W., Environ. Sc. Technol., **1999**, *33*
16. Rao, P. S.; Hayon, E., *J. Phys. Chem*. **1973**, *77*, 275
17. Arikan, B.; Micellar, M. T., *Dyes Pigm*. **2005**, *64*, 1–8
18. Christopher, S., *Science* **1968**, *162*, 3857
19. Chibisov, K.; Slavnova, T. D.; Zakharova, G. V.; Grner, H., *High Energy Chem*. **2007**, *41*, 344–349
20. Somer, G.; Temizer, A., *Photochem. Photobiol*. **1984**, *40*, 575–580
21. Chen, C.; Li, X.; Ma, W.; Zhao, J.; Hidaka, H.; Serpone, N., *Phys. Chem. B* **2002**, *106*, 318–324
22. Lilani, M. D.; Sharma, G. K.; Shanker, R., *Indian J. Chem*. **1986**, *25*(*A*), 370 (s)