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PHOTOCHEMICAL METHOD FOR ESTIMATION OF THIOUREA USING SODIUM NITROPRUSSIDE

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ABSTRACT

A newer fast, convenient and inexpensive quantitative method for the determination of thiourea using photochemical exchange reaction of sodium nitroprusside has been investigated. Sodium nitroprusside is a photolabile complex and it undergoes photochemical ligand exchange reactions rapidly. Some efforts have been made to utilise such reactions for the estimation of some sulphur containing anions and electron rich organic molecules. The progress of the reaction has been observed spectrophotometrically. The effects of different parameters like pH, change of concentration of sodium nitroprusside, concentration of ligands, light intensity etc. on percentage error was investigated. The efforts were made to minimise the percentage error and some optimum conditions were obtained. Such reaction can be used for the determination of thiourea in the range of millimoles to micromoles and hence, it is important to know whether such estimations can be done successfully and that to with the desired accuracy.

Key words: Photochemical exchange reaction, Sodium nitroprusside, Quantitative, Thiourea, percentage error.

INTRODUCTION

The essential feature of photochemistry is probably the way in which the excited states of the atoms or molecules play a part in process of interest. It is apparent that the absorption or emission of radiation to/from these states is the concern of spectroscopists as well as the photochemists. Photosensitized reactions are widely used in many technical and biological areas. Organic chemists may seek an improved understanding through photochemistry, which gives a relationship between reactivity and electronic and molecular

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structure[1]. Photosensitized reactions like copolymerization have been reported by Burrows *et al.*[2]

Photoreduction of water has also been investigated using Wilkinson type complex, $[RhCl(dpm)_3]^{-3}$. It has been used as homogeneous catalyst in conjunction with $[Ru(bpy)_3]^{+2}$ and ascorbic acid by Oishi[3]. Ziessel *et al.*[4] have reported that carbon monoxide and hydrogen can be produced by the simultaneous photochemical reduction of CO_2 and H_2, when solution containing $[Ru(bpy)_3]^{+2}$ and different Co (II) species were irradiated with visible light. The photocatalytic oxidation of ascorbic acid with the evolution of hydrogen by platinum loaded TiO_2-$[Ru(bpy)_3]^{+2}$ system was observed by Taqui Khan *et al.*[5]

Haeven *et al.*[6] have carried out the electrochemical characterization of freshly prepared NiC_2O_4 electrodes for oxygen evolution, whereas, Yoon and Kim[7] made a comparison of photoeffects in doped and undoped $SrTiO_3$ ceramic electrodes. Belousov *et al.*[8] studied the photocatalytic properties of homogeneous colloids and heterogeneous vanadium containing system (in ethanol). The photocatalytic cyclisation of 7-styryl-1-H-pyrol-(2,6)-pyridiuinium bromide was investigated by Ogali and Walker[9]. The effect of inorganic anions on the TiO_2 based photocatalytic oxidation of aqueous ammonia and nitrite was reported by Zhu *et al.*[10] Photodegradative treatment of waste water by U.V./TiO_2 process was investigated by Liu *et al.*[11] Photodecomposition of ammonia to dinitrogen and dihydrogen on Pt/TiO_2 nanoparticles in an aqueous solution was studied by Nemono *et al.*[12].

A comparison between TiO_2 and Fenton plus photo-Fenton reaction in a solar pilot plant was reported by Maldonado *et al.*[13] Matsuo and Udea[14] used TiO_3-TiO_2 composite powder for the photocatalytic bleaching of methylene blue. Photocatalytic degradation and adsorption of di-isopropyl fluorophosphate and dimethyl phosphonate over dry and wet rutile TiO_2 was studied by Kiselev *et al.*[15]. Physicochemical and photocatalytic characterization of TiO_2 /Pt nanoparticles has been made by Liu *et al.*[16] Yuan *et al.*[17] observed Fe assisted photocatalytic degradation of microcystin- LR using titanium dioxide. Photodegradation and adsorption of 1,4-dioxane on TiO_2 was carried by Yamazaki *et al.*[18].

EXPERIMENTAL

A 100 mL stock solution of thiourea (M/100) and 100 mL stock solution of sodium nitroprusside (M/100) (SNP) were prepared by dissolving 0.07612 g of thiourea and 0.2979 g of sodium nitroprusside in doubly distilled water. 20 mL of stock sodium nitroprusside solution was diluted to 100 mL to form M/500 concentration and then it was divided into five equal parts (20 mL each). In each beaker, the solution of thiourea (M/100) was mixed as 0.4 mL, 0.8 mL, 1.2 mL, 1.6 mL and 2.0 mL and all the beakers were exposed to a 200 watt tungsten lamp for 15 minutes. A change in colour of solution was observed from light red to peacock blue.

An aliquot of 5.0 mL solution was taken out from each reaction mixture and change in optical density was observed spectrophotometrically at λ_{max} = 380 nm.

A graph was plotted between optical density and known concentrations of thiourea i.e. [1.96×10^{-4} M, 2.91×10^{-4} M, 3.84×10^{-4} M, 5.66×10^{-4} M, 7.42×10^{-4} M, 8.23×10^{-4} M]. A straight line was obtained, which was used later on as a calibration curve. 1.0 mL sample solution of known thiourea concentration was mixed in 20 mL of sodium nitroprusside (M/500) and it was exposed to tungsten lamp under identical conditions. The optical density was measured spectrophotometrically and the concentration of sample solution was determined by the calibration curve. From this, the concentration was determined and the percentage error was calculated for thiourea sample solution.

RESULTS AND DISCUSSION

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of thiourea may be affected by the variation in pH value and as such the estimation of thiourea may also be affected accordingly. Therefore the effect of pH on quantitative estimation of thiourea was studied at different pH values. The results are reported in Table 1.

Table 1. Effect of pH

[SNP] = 6.6×10^{-3} M [Thiourea] = 4.0×10^{-3} M

Light Intensity = 14.0 mWcm^{-2} λ_{max} = 380 nm

pH	Error (%)
2.0	10.7
2.5	10.3
3.0	9.5
3.5	8.7

Cont…

pH	**Error (%)**
4.0	8.0
4.5	5.6
5.0	4.3
5.5	3.3
6.0	2.7
6.5	2.1
7.0	1.8
7.5	1.9
8.0	2.1
8.5	2.5
9.0	3.0
9.5	3.5
10.0	4.2
10.5	5.1
11.0	6.0

It was observed that the minimum error in the estimation of thiourea was found at pH = 7 i.e. only 1.8 %, which is within permissible limits. Below pH = 7.0, thiourea exists in the form of protonated cation and above pH = 7.0 value, the % error increases indicating that complex formation between thiourea and sodium nitroprusside only partially completed. It seems that the neutral form of thiourea acts as good ligand than its anionic and cationic form.

Effect of thiourea concentration

The effect of the concentration of thiourea on the estimation was also observed by taking different concentrations of thiourea, keeping all other factors identical. The results are reported in Table 2.

Table 2. Effect of thiourea concentration

[SNP] = 6.6 x 10^{-3} M pH = 7.0

Light Intensity = 14.0 $mWcm^{-2}$ λ_{max} = 380 nm

[Thiourea] x 10^3 M	**Error (%)**
2.00	3.5
2.10	3.5
2.20	3.4
2.30	3.2
2.50	3.0
2.70	2.8
2.80	2.7
3.00	3.1
3.30	2.4
3.60	2.2
4.00	1.8
4.40	2.1
4.46	2.1
5.00	2.4
5.50	2.7
5.80	2.9
6.25	3.2
6.60	3.6
7.10	4.1

It was observed that the minimum error in the estimation of thiourea was found at thiourea concentration 4.0 x 10^{-3}M.

As the concentration of thiourea was increased, the complex formation tendency also increases and hence, the percentage error found in estimation of thiourea is minimum but as the concentration was increased higher than 4.0 x 10^{-3} M, there may be possibility of some larger units and 2 or more than 2 molecules of thiourea bind together through intermolecular hydrogen bonding. Such a unit will not participate in complex formation due to its larger size and lower nucleophilicity and therefore, limited complex formation takes place resulting into increase in error at higher concentrations of thiourea.

Effect of sodium nitroprusside concentration

The effect of variation of concentration of sodium nitroprusside on the quantitative estimation of thiourea and percentage error was observed by taking different concentrations of sodium nitroprusside and keeping all other factors identical. The results are reported in Table 3.

Table 3. Effect of sodium nitroprusside concentration

[Thiourea] = 4.0 x 10^{-3} M pH = 7.0

Light Intensity = 14.0 mWcm^{-2} λ_{max} = 380 nm

[SNP] x 10^3 M	Error %
3.30	5.50
4.00	4.40
4.40	3.70
5.00	3.10
5.50	2.50
5.80	2.30
6.25	2.05
6.60	1.80
7.10	2.20
7.60	2.60
8.30	3.40
9.00	3.70
10.0	4.80

It was found that the minimum error in the estimation of thiourea was found at sodium nitroprusside concentration 6.6 x 10^{-3} M. As the concentration of sodium nitroprusside was increased the complex formation tendency increases, it reaches maximum at sodium nitroprusside concentration 6.6 x 10^{-3} M but if the concentration was further increased, it will start acting like an internal filter and it will not permit the desired light intensity to reach sodium nitroprusside molecule in the bulk of the solution, and as a consequence, only limited number of sodium nitroprusside molecules will be excited to participate in the complex formation resulting into increase in percentage error.

Effect of light intensity

The effect of light intensity on the percentage error in the estimation of thiourea by its photochemical reaction with sodium nitroprusside has been observed by varying the distance between the exposed surface of the reaction mixture and tungsten lamp (light source). The results are tabulated in Table 4.

Table 4. Effect of light intensity

[Thiourea] = 4.0 x 10^{-3} M pH = 7.0

[SNP] = 6.6 x 10^{-3} M λ_{max} = 380 nm

Light Intensity (mWcm^{-2})	Error (%)
6.0	4.5
7.0	4.1
8.0	3.7
9.0	3.2
10.0	2.6
11.0	2.4
12.0	2.2
13.0	2.0
14.0	1.8
15.0	1.8
16.0	1.8

It has been observed that the minimum error in the estimation of thiourea was found at light intensity = 14.0 mWcm^{-2}.

As the light intensity was increased, the number of photons striking per unit area per second will also increase. As a result, the complex formation became little bit easier on increasing light intensity. On further increasing the light intensity beyond 15.0 $mWcm^{-2}$, the error remains almost constant indicating that the desired light intensity for maximum (complete) formation of complex requires this much intensity and any increase will not increase the amount of complex formed. This will result into a constant error above this intensity.

Optimum conditions

The photochemical reaction between sodium nitroprusside and thiourea was carried out. It was observed that if the estimation of thiourea is carried out under these given conditions, the percentage error observed is minimum (1.8%) and it is within permissible limits.

The optimum conditions are –

(i) pH = 7.0

(ii) [Sodium Nitroprusside] = 6.6×10^{-3} M

(iii) [Thiourea] = 4.0×10^{-3} M

(iv) Light Intensity = 14.0 $mWcm^{-2}$

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