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ESTIMATION OF SEMICARBAZIDE USING SODIUM NITROPRUSSIDE BY A NEWER PHOTOCHEMICAL METHOD

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ABSTRACT

Determination of semicarbazide using photochemical exchange reaction of sodium nitroprusside has been investigated. It is an inexpensive, faster and convenient quantitative method. Sodium nitroprusside is a photolabile complex, which undergoes photochemical ligand exchange reactions rapidly. Some recent efforts have been made to utilise such reactions for the estimation of some nitrogen containing anions and electron rich organic molecules. The progress of the reaction is 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 optimum conditions were obtained. Such reaction can be used for the determination of semicarbazide in the range of millimoles to micromoles; and that too with the desired accuracy.

Keywords: Semicarbazide, Sodium nitroprusside, Photochemical exchange reaction, Quantitative, Percentage error, Optimum conditions.

INTRODUCTION

Photochemistry plays a pivotal role in a number of chemical and biological processes. Photochemistry of biological reactions is a rapidly developing subject and helps in understanding phenomena like photosynthesis, phototaxis, photoporiodism, photodynamic action, vision and mutagenic photoeffect of light.

Photochemistry is the chemistry of excited electronic states of molecules. An electronic excitation is simply regarded as a process, whereby an electron is removed from

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an orbital with certain bonding characteristics and reinserted in another orbital with different characteristics and these excited states are generated by excitation of compounds, atoms or molecules using appropriate wavelengths in the ultraviolet or visible region of the spectrum. 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.

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*.[1] Belousov *et al*.[2] studied the photocatalytic properties of homogeneous colloids and heterogeneous vanadium containing system (in ethanol). Photodegradative treatment of waste water by U.V./TiO_2 process was investigated by Liu *et al*.[3]. Otsuka and Udea[4] used TiO_3-TiO_2 composite powder for the photocatalytic bleaching of methylene blue. Nemono *et al*.[5] studied photodecomposition of ammonia to dinitrogen and dihydrogen on Pt/TiO_2 nanoparticles in an aqueous solution.

Photodegradation and adsorption of 1,4-dioxane on TiO_2 was carried by Yamazaki *et al*.[6] Chen *et al*.[7] studied photocatalytic oxidation of aromatic aldehydes with Co (II)-tetra-(benzoyl-oxyphenyl) prophyrin and molecular oxygen. Sarkha *et al*.[8] investigated the selective oxidation of meta- and para-phenylphenol photosensitized by $[Co(NH_3)_5N_3]^{2+}$ in aqueous solution. The photoexcitation kinetics of octacyano complexes of Mo (IV) and W (IV) with ethylene diamine were studied by Ali and Kaur[9], while kinetic studies of octacyano complexes of Mo (IV) and W (IV) with ethanol amine was studied by Ali and Majid[10].

A comparison between TiO_2 and Fenton plus photo-Fenton in a solar pilot plant was reported by Maldonado *et al*.[11] Connik and Gray[12] investigated photooxidation of platinum (II) diaminedithiolates, whereas, photosubstitution and photoredox behavior of cyanometallates and reaction models were examined by Sfasicka and Wasielewska.[13] The effect of inorganic anions on the TiO_2 based photocatalytic oxidation of aqueous ammonia and nitrite was reported by Zhu *et al*.[14]. Photochemical and spectroscopic properties of solutions of Pt (II) complex with bis(salicylidene) ethylenediamine were observed by Shagisultanova and Ardashova[15].

Yu and Chuang[16] studied the adsorbed species and photogenerated electrons during photocatalytic oxidation of ethanol on TiO_2 whereas photocatalytic transformation of acid orange 20 and Cr (VI) in aqueous TiO_2 suspensions was studied by Papadam *et al*.[17]. Zhang and Maggard[18] investigated photocatalytically active hydrated forms of amorphous titania, $TiO_2.nH_2O$. Photodegration of rhodamine B in aqueous solution via SiO_2 - TiO_2 nanospheres was reported by Wilhelm and Stephanwhile[19]. Wachter *et al.*[20] observed the photochemical reactivity of a dye precursor 4-chloro-1, 2-phenylenediamine. They also studied the mutagenic effects of this precursor. The photodegradation of arylmethane and azo dyes over TiO_2/In_2O_3 nano composite films was reported by Skorb *et al.*[21] Photocatalytic degradation of acetaldehyde over TiO_2 pellets was carried out by Horikoshi *et al.*[22] Sun *et al.*[23] reported the photocatalytic activity of titanium cobalt oxides in the degradation of methyl orange. High photocatalytic activity of Fe-doped TiO_2 nano tubes was observed by Deng *et al.*[24] Chen *et al.*[25] observed the activities of different metal oxide as photocatalyst on reduction and cooxidation. Photocatalytic hydrogen production from aqueous solutions of alcohol using visible light responsive TiO_2 thin films was reported by Fukumoto *et al.*[26] Srinivas *et al.*[27] observed photooxidation of beta-picoline to nicotinic acid over vanadia/titania catalyst .The photocatalytic properties of TiO_2 nano tubes coated with gold was observed by Malwadkar *et al.*[28] Asilturk *et al.*[29] reported the effect of Fe^{3+} ion doped TiO_2 on the photodegradation of malachite green dye under UV-visible irradiation. Zita *et al.*[30] investigated the correlation between photooxidation and photoreduction of dyes over TiO_2 films.

EXPERIMENTAL

A 100 mL stock solution of semicarbazide (M/100) and 100 mL stock solution of sodium nitroprusside (SNP) (M/100) were prepared by dissolving 0.01115 g of semicarbazide and 0.2979 g of sodium nitroprusside in doubly distilled water, respectively. 20 mL of stock sodium of 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 (M/100) semicarbazide 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 orange to pink. 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} = 385 nm.

A graph was plotted between optical density and known concentrations of semicarbazide 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 as a calibration curve. 1.0 mL sample solution of known semicarbazide 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 determined concentration, the percentage error was calculated for different semicarbazide sample solutions.

RESULTS AND DISCUSSION

Effect of pH

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

Table 1: Effect of pH

[SNP] = 2.5×10^{-3} M [Semicarbazide] = 5.4×10^{-3} M

Light intensity = 15.0 $mWcm^{-2}$ λ_{max} =385 nm

pH	Error (%)
5.5	10.0
6.0	8.6
6.5	7.9
7.0	5.6
7.5	**1.9**
8.0	3.6
8.5	4.3
9.0	5.8
9.5	7.7

It was observed that the minimum error in the estimation of semicarbazide is found at pH = 7.5 i.e. only 1.9 %, which is within permissible limit. Below pH = 7.5, semicarbazide exists in the form of protonated cation and above pH = 7.5 value, the % error increases indicating that complex formation between semicarbazide and sodium nitroprusside is completed partially. It seems that the anionic form of semicarbazide acts as good ligand than its cationic form.

Effect of semicarbazide concentration

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

Table 2: Effect of semicarbazide concentration

[SNP] = 2.5 x 10^{-3} M pH = 7.5

Light intensity = 15.0 $mWcm^{-2}$ λ_{max} = 385 nm

[Semicarbazide] x 10^3 M	Error (%)
1.8	7.5
2.0	5.8
2.2	5.6
2.5	5.4
2.8	4.8
3.3	3.9
4.0	3.2
4.5	2.8
5.0	2.6
5.4	**1.9**
6.0	2.2
6.6	2.4
8.5	2.9
10.0	3.4
13.3	4.2

It was observed that the minimum error in the estimation of semicarbazide is found at semicarbazide concentration 5.4 x 10^{-3} M i.e. only 1.9 %, which is within permissible limit. As the concentration of semicarbazide was increased, the complex formation tendency increases and hence, the percentage error in estimation of semicarbazide was found minimum but as the concentration was increased higher than 5.4 x 10^{-3}M, there may be possibility of some larger units 2 or more than 2 molecules of semicarbazide 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 concentration of semicarbazide.

Effect of sodium nitroprusside concentration

The effect of variation of concentration of sodium nitroprusside on the quantitative estimation of semicarbazide 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

[Semicarbazide] = 5.4 x 10^{-3} M pH = 7.5

Light Intensity = 15.0 $mWcm^{-2}$ λ_{max} = 385 nm

[SNP] x 10^3 M	Error %
1.6	5.3
1.8	4.4
2.0	3.2
2.2	2.1
2.5	**1.9**
2.8	2.2
3.3	2.6
4.0	2.8
5.0	3.1
6.6	4.2
10.0	5.2

Minimum error in the estimation of semicarbazide was found at sodium nitroprusside concentration 2.5 x 10^{-3} M i.e. only 1.9 %, which is within permissible limit. As the concentration of sodium nitroprusside was increased, the complex formation tendency increases and it reaches maximum at sodium nitroprusside concentration 2.5 x 10^{-3}M but if the concentration is further increased, then 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. 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 semicarbazide while 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 result for tungsten lamp are tabulated in Table 4

Table 4: Effect of light intensity

[Semicarbazide] = 5.4 x 10^{-3} M pH = 7.5

[SNP] = 2.5 x 10^{-3} M λ_{max} =385 nm

Light Intensity (mWcm^{-2})	**Error (%)**
6.0	5.9
7.0	5.1
8.0	4.5
9.0	3.8
10.0	3.2
11.0	2.7
12.0	2.4
13.0	2.1
14.0	2.0
15.0	1.9
16.0	1.9

It is observed that the minimum error in the estimation of semicarbazide was found at light intensity = 15.0 mWcm^{-2} i.e. only 1.9 %, which is within permissible limit. 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 16.0 mWcm^{-2}, the error remains almost constant indicating that the desired light intensity for maximum (complete) formation of complex requires this much intensity only and any increase in light intensity 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 semicarbazide was carried out. It was observed that if the estimation of semicarbazide is carried out under these given conditions, then the percentage error observed is minimum (1.9%) and within permissible limit.

The optimum conditions are given below –

(i) pH = 7.5

(ii) [Sodium Nitroprusside] = 2.5 x 10^{-3}M

(iii) [Semicarbazide] = 5.4 x 10^{-3}M

(iv) Light Intensity = 15.0 mWcm^{-2}

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