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A NEWER PHOTOCHEMICAL METHOD FOR ESTIMATION OF p-PHENYLENE DIAMINE USING SODIUM NITROPRUSSIDE

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ABSTRACT

A newer, faster, inexpensive and convenient quantitative method for the determination of p-phenylene diamine 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 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 some optimum conditions were obtained. Such reaction can be used for the determination of p-phenylene diamine in the range of millimoles to micromoles, hence it is important to know whether such estimations can be done successfully and that to with the desired accuracy.

Keywords: photochemical exchange reaction, p-phenylene diamine, sodium nitroprusside, quantitative, percentage error, optimum conditions.

INTRODUCTION

Photochemistry of biological reactions is a rapidly developing subject and helps in understanding of phenomena like Photosynthesis, Phototaxis, Photoperiodism, Photodynamic action, vision and mutagenic photo effect of light. Photochemistry plays a pivotal role in a number of chemical and biological processes. Photosensitized reactions are widely used in many technical and biological areas. Photosynthesis is such an important photochemical reaction controlled by nature, which still exists as a challenge to the photochemists. Generally 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 an orbital with certain bounding 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.

Photodegradative treatment of waste water by U.V./TiO₂ process was investigated by Liu *et al.*¹. Photodegradation and adsorption of 1,4-dioxane on TiO₂ was carried by Yamazaki *et al.*². The photoexcitation kinetics of octacyano complexes of Mo(IV) and W(IV) with ethylene diamine were studied by Ali and Kaur³, while kinetic studies of octacyano complexes of Mo(IV) and W(IV) with ethanol amine was studied by Ali and Majid⁴.

A comparison between TiO₂ and Fenton plus photo-Fenton in a solar pilot plant was reported by Maldonado *et al.*⁵. Connik and Gray⁶ investigated photooxidation of Platinum (II) diaminedithiolates,

whereas, photosubstitution and photoredox behavior of cyanometallates and reaction models were examined by Sfasicka and Wasielewska⁷.

The effect of inorganic anions on the TiO₂ based photocatalytic oxidation of aqueous ammonia and nitrite was reported by Zhu *et al.*⁸. Otsuka and Udea⁹ used TiO₃-TiO₂ composite powder for the photocatalytic bleaching of methylene blue. Nemono *et al.*¹⁰ studied photodecomposition of ammonia to dinitrogen and dihydrogen on Pt/TiO₂ nanoparticles in an aqueous solution. Yu & Chuang¹¹ studied the adsorbed species and photogenerated electrons during photocatalytic oxidation of ethanol on TiO₂ whereas photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous TiO₂ suspensions was studied by Papadam *et al.*¹².

Zhang & Maggard¹³ investigated photocatalytically active hydrated forms of amorphous titania, TiO₂ center dot nH₂O. Photodegradation of Rhodamine B in aqueous solution via SiO₂ - TiO₂ nano-spheres was reported by Wilhelm and Stephanwhile¹⁴. Photocatalytic degradation of acetaldehyde over TiO₂ pellets was carried out by Horikoshi *et al.*¹⁵. Wachter *et al.*¹⁶ 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 TiO₂/In₂O₃ nano composite films reported Skorb *et al.*¹⁷.

Sun *et al.*¹⁸ reported the photocatalytic activity of titanium cobalt oxides in the degradation of methyl orange. Chen *et al.*¹⁹ showed the activities of different metal oxide as photocatalyst on no reduction and cooxidation. High photocatalytic activity of Fe-doped TiO₂ nano tubes was observed by Deng *et al.*²⁰. Asilturk *et al.*²¹ reported the effect of Fe³⁺ ion doped TiO₂ on the photodegradation of malachite green dye under UV-visible irradiation. Photochemical and spectroscopic properties of solutions of Pt(II) complex with bis(salicylidene) ethylenediamine were observed by Shagisultanova and Ardashova²². Photocatalytic hydrogen production from aqueous solutions of alcohol using visible light responsive TiO₂ thin films was reported by Fukumoto *et al.*²³. Srinivas *et al.*²⁴ observed photooxidation of beta picoline to nicotinic acid over vanadia/titania catalyst. Zita *et al.*²⁵ investigated the correlation between photooxidation and photoreduction of dyes over TiO₂ films. The photocatalytic properties of TiO₂ nano tubes coated with gold was given by Malwadkar *et al.*²⁶.

EXPERIMENTAL

A 100 mL stock solution of p-phenylene diamine (M/100) and 100 mL stock solution of sodium nitroprusside [SNP] (M/100) were prepared by dissolving 0.01081g of p-phenylene diamine and 0.2979g 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 (M/100) p-phenylene diamine 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 light blue. An aliquot of 5.0 mL solution was taken out from each reaction mixture and change in optical density was observed spectrophotometrically at $\lambda_{\max} = 380$ nm.

A graph was plotted between optical density and known concentration of p-phenylene diamine i.e. [1.96 x 10⁻⁴ M, 2.91 x 10⁻⁴ M, 3.84 x 10⁻⁴ M, 5.66 x 10⁻⁴ M, 7.42 x 10⁻⁴ M, 8.23 x 10⁻⁴ M]. A straight line was obtained, which was used later on as a calibration curve. 1.0 mL sample solution of known p-phenylene diamine 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 p-phenylene diamine sample solution.

RESULTS AND DISCUSSION

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of p-phenylene diamine may be affected by the variation in pH value and as such the estimation of p-phenylene diamine may also be affected

accordingly. Therefore the effect of pH on quantitative estimation of p-phenylene diamine was studied at different pH range. The results are reported in Table -1.

It was observed that the minimum error in the estimation of p-phenylene diamine is found at pH=7.0 i.e. only 1.7 % which is within permissible limit. Below pH =7.0, p-phenylene diamine exists as form of protonated cation and above pH = 7.0 value, the % error increases indicating that complex formation between p-phenylene diamine and sodium nitroprusside partially completes. It seems that the cationic form of p-phenylene diamine acts as good ligand than its anionic form.

Table-1: Effect of pH

[SNP] = 2.8×10^{-3} M Light intensity = 14.0 mWcm^{-2}	[p-phenylene diamine] = 6.6×10^{-3} M $\lambda_{\text{max}} = 380 \text{ nm}$
pH	Error (%)
2.5	8.6
3.0	8.2
3.5	7.7
4.0	6.4
4.5	4.8
5.0	4.0
5.5	3.2
6.0	2.8
6.5	2.5
7.0	1.7
7.5	2.6
8.0	3.2
8.5	4.1
9.0	5.3
9.5	6.1

Effect of p-Phenylene Diamine Concentration

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

Table-2: Effect of p-Phenylene Diamine Concentration

[SNP] = 2.8×10^{-3} M Light intensity = 14.0 mWcm^{-2}	pH = 7.0 $\lambda_{\text{max}} = 380 \text{ nm}$
[p-phenylene diamine] x 10^3 M	Error (%)
2.0	10.5
2.5	9.8
3.3	8.4
4.0	6.9
4.5	5.7
5.0	4.6
5.4	3.5
5.7	2.8
6.0	2.2
6.6	1.7
7.0	2.0

7.6	2.4
8.5	4.9
10.0	8.4
12.5	11.0

It was observed that the minimum error in the estimation of p-phenylene diamine is found at p-phenylene diamine concentration 6.6×10^{-3} M i.e. only 1.7 % which is within permissible limit. As the concentration of p-phenylene diamine increases the complex formation tendency increases and hence the percentage error found in estimation of p-phenylene diamine is minimum but as the concentration is increased higher than 6.6×10^{-3} M there may be possibility of some larger units (2 or more than 2 molecules) of p-phenylene diamine bind together through intermolecular hydrogen bonding. Such a unit will not participate in complex formation due to its larger size and lower nucleophilicity, therefore limited complex formation takes place resulting into increase in error at higher concentration of p-phenylene diamine.

Effect of Sodium Nitroprusside Concentration

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

Table-3: Effect of Sodium Nitroprusside Concentration

[p-phenylene diamine] = 6.6×10^{-3} M Light Intensity = 14.0 mWcm^{-2} [SNP] $\times 10^3$ M	pH = 7.0 $\lambda_{\text{max}} = 380 \text{ nm}$ Error %
1.5	6.3
1.8	5.4
2.0	4.7
2.2	3.5
2.5	2.3
2.8	1.7
3.3	2.5
4.0	3.2
5.0	4.4
6.6	5.2
10.0	9.2
12.5	11.2

It was found that the minimum error in the estimation of p-phenylene diamine is found at sodium nitroprusside concentration 2.8×10^{-3} M i.e. only 1.7 %, which is within permissible, limit. As the concentration of sodium nitroprusside increases the complex formation tendency increases, it reaches maximum at sodium nitroprusside concentration 2.8×10^{-3} M but if the concentration is further increased it will start acting like a 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 molecule 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 p-phenylene diamine 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 results are tabulated in Table-4.

It is observed that the minimum error in the estimation of p-phenylene diamine is found at light intensity = 14.0 mWcm⁻² i.e. only 1.7 % 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 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.

Table- 4: Effect of Light Intensity

[p-phenylene diamine] = 6.6 x 10 ⁻³ M [SNP] = 2.8 x 10 ⁻³ M Light Intensity (mWcm ⁻²)	pH = 7.0 λ_{\max} = 380 nm Error (%)
6.0	7.2
7.0	6.1
8.0	5.9
9.0	4.1
10.0	3.2
11.0	2.7
12.0	2.3
13.0	2.0
14.0	1.7
15.0	1.7
16.0	1.7

CONCLUSIONS

The photochemical reaction between sodium nitroprusside and p-phenylene diamine was carried out. It was observed that if the estimation of p-phenylene diamine is carried out under these given conditions the percentage error observed is minimum (1.7 %) and within permissible limit.

The optimum conditions are given below:-

1. pH = 7.0
2. [Sodium Nitroprusside] = 2.8 x 10⁻³ M
3. [p-phenylene diamine] = 6.6 x 10⁻³ M
4. Light Intensity = 14.0 mWcm⁻²

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