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Research Article

Estimation of Cystiene Using Sodium Nitroprusside by a Newer Photochemical Method

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Abstract: A newer fast, convenient and inexpensive quantitative method for the determination of Cystiene 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 sulphur 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 Cystiene 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, sodium nitroprusside, quantitative, Cystiene, percentage error.

INTRODUCTION

Photochemistry plays a pivotal role in a number of chemical and biological processes. Photosynthesis is such an important photochemical reaction controlled by nature, which still exists as a challenge to the photochemists. 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 chemist may seek an improved understanding through the example that photochemistry gives the relationship between reactivity and electronic and molecular structure[1]. Photosensitized reactions like copolymerization have been reported by Wayne and Burrows et al.[2].

Cysteine is a sulphur containing amino acid and it is presented in the form of its oxidized product cysteine. In this form, the disulphide cross links may be intra or intermolecular. The thiol group of Cysteine is active and it is blocked by a wide range of aralkyl. The commonly used blocking groups are Benzyl[3], diphenyl methyl[4], and triphenylmethyl[5,6]. Cysteine is a major metal binding sites in proteins as a ligand, it shows ambidentate behaviour and can be tridentate or bidentate through coordination of (S,N,O) (S,N) (N,O) or (S,O) donor atoms. The strong affinity of soft metal ions for ionized thiol groups also gives rise to monodentate behaviour. The thiol anion is also a very effective metal binding site. Some of the known modes of binding of cysteine to various metal ions is given in Table-III . A number of cysteine complexses have been studied and it seems that at least two functional groups on the liagnd[7] are utilized for binding it to the metal atom. One of these must be sulphur, while the other may be –COOH or NH_2[8]. Cysteine has been used as a detoxicant and as dough conditioner.

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.[9]. Belousov et al.[10] studied the photocatalytic properties of homogeneous colloids and heterogenous vanadium containing system (in etahnol). The photocatalytic cyclisation of 7-styryl-1-H-pyrool-(2,6)-pyridiuinium bromide was investigated by Ogali and Walker[11].The effect of inorganic anions on the TiO_2 based photocatalytic oxidation of aqueous ammonia and nitrite was reported by Zhu *et al.*[12].

A comparison between TiO_2 and Fenton plus photo-Fenton 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]. Physiochemical 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].

Photocatalytic selective oxidation of methanol to methyl formate in gas phase over titanium (IV) oxide in a flow-type reactor was reported by Kominami *et al.* [19]. Lv *et al.*[20] synthesized floriated $ZnFe_2O_4$ with porous nanorod structures and determined its photocatalytic hydrogen production ability under visible light. Role of defects and paramagnetic species in solar photoactivity of nano-N-TiO_2 from tertiary amine was reported by Spadavecchia *et al.*[21]. Effect of light source on the catalytic degradation of protocatechuic acid in a ferrioxalate-assisted photo-Fenton process was observed by Monteagudo *et al.*[22]. Lo *et al.*[23] manufactured novel twin reactor to separate evolution of hydrogen and oxygen in photocatalytic water splitting. Photocatalytic oxidation for antimicrobial control in built environment was studied by Chen *et al.*[24].

EXPERIMENTAL

A 100 mL stock solution of Cysteine (M/100) and 100 mL stock solution of sodium nitroprusside (M/100) were prepared by dissolving 0.1210g of Cysteine 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) Cysteine was mixed as 0.4 mL, 0.8 mL, 1.2mL, 1.6mL and 2.0 mL and all the beakers were exposed to a 200 watt tungsten lamp for 13 minutes. A change in colour of solution was observed from light red to pale yellow.

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} = 310 nm. A graph was plotted between optical density and known concentration of Cysteine 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 Cysteine 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 Cysteine sample solution.

EFFECT OF PH

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

Table -1: Effect of PH

[SNP] = 6.3 x 10^{-3} M	[Cysteine] = 2.5 x 10^{-3} M
Light Intensity = 14.0 mWcm^{-2}	λ_{max} = 310 nm
pH	**Error (%)**
4.0	3.5
4.5	3.2
5.0	3.1
5.5	2.7
6.0	2.2
6.5	1.0
7.0	2.0
7.5	2.3
8.0	2.5
8.5	2.5
9.0	3.0
9.5	3.2
10.0	3.2
10.5	3.4
11.0	3.5

It was observed that the minimum error in the estimation of Cysteine is found at pH = 6.5 i.e. only 1.0% which is within permissible limit. Below pH = 6.5 cysteine remains in protonated form, which is not good donor whereas on other hand pH higher than 7, it remains in anionic form, but the percentage error is high in alkaline range indicating that it is not a good donor in spite of being negatively charged. The results indicate that cysteine replaces some ligands from the coordination sphere of iron easily in the form of zwitter ion to form the complex.

EFFECT OF CYSTEINE CONCENTRATION

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

Table -2: Effect of Cysteine Concentration

[SNP] = 6.3 x 10^{-3} M	pH = 6.5
Light Intensity = 14.0 mWcm^{-2}	λ_{max} = 310 nm
[Cysteine] x 10^3 M	**Error (%)**
1.0	3.0
1.4	2.7
1.5	2.5
1.6	2.5
1.8	2.3
2.0	2.0
2.2	1.5
2.5	1.0
2.8	1.5
3.3	2.0
4.0	2.5
5.0	3.0
6.6	3.5

It was observed that the minimum error in the estimation of Cysteine is found at Cysteine concentration 2.5 x 10^{-3}M i.e. only 1.0% that is within permissible limit. As the concentration of Cysteine increases the complex formation tendency increases and hence the percentage error found in estimation of Cysteine is minimum but as the concentration is increased higher than 2.5 x 10^{-3}M there may be possibility of some larger units 2 or more than 2 molecules of Cysteine 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 Cysteine.

EFFECT OF SODIUM NITROPRUSSIDE CONCENTRATION

The effect of variation of concentration of sodium nitroprusside on the quantitative estimation of Cysteine 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.**It was found that the minimum error in the estimation of Cysteine is found at sodium nitroprusside concentration 6.3 x 10^{-3}M i.e. only 1.0%, which is within permissible limit. As the concentration of sodium nitroprusside increases the complex formation tendency increases, it reaches maximum at sodium nitroprusside concentration 6.3 x

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.

Table- 3: Effect of Sodium Nitroprusside Concentration

[Cysteine] = 2.5 x 10^{-3} M	pH = 6.5
Light Intensity = 15.0 mWcm^{-2}	λ_{max} = 310 nm
[SNP] x 10^{-3} M	Error (%)
3.0	4.5
3.3	4.0
4.0	3.5
4.4	2.7
5.0	2.2
5.5	2.0
5.8	1.5
6.3	1.0
6.6	1.5
7.1	2.1
7.6	2.5
8.3	3.5
9.0	4.5
10.0	4.5

EFFECT OF LIGHT INTENSITY

The effect of light intensity on the percentage error in the estimation of Cysteine 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

[Cysteine] = 2.5 x 10^{-3} M	pH = 6.5
[SNP] = 6.3 x 10^{-3} M	λ_{max} = 310 nm
Light Intensity (mWcm^{-2})	**Error (%)**
6.0	3.5
7.0	3.2
8.0	2.8
9.0	2.5
10.0	1.7
11.0	1.5
12.0	1.2
13.0	1.0
14.0	1.0
15.0	1.0
16.0	1.0

It is observed that the minimum error in the estimation of Cysteine is found at tungsten lamp intensity = 13.0 $mWcm^{-2}$ i.e. only 1.0% 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 13.0 $mWcm^{-2}$ 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 Cysteine was carried out. It was observed that if the estimation of Cysteine is carried out under these given conditions the percentage error observed is minimum (1.0 %) and within permissible limit.

The optimum conditions are given below:

(i) pH = 6.5

(ii) [Sodium Nitroprusside] = 6.3×10^{-3}M

(iii) [Cysteine] = 2.5×10^{-3}M

(iv) Light Intensity = 13.0 $mWcm^{-2}$

REFERENCES

1. K.K. Rohatagi, Mukherji, Fundamental of Photochemistry Wiley Eastern Limited, New Delhi,1997.
2. H.D. Burrows, S. J. Formosinho and P.M. Sarvaiva, J. Photochem. Photobiol.,1992, **63A**, 75.
3. R. H. Sifferd and V. Du. Vigenand, J. Biol. Chem., 1935,**108**, 753.
4. L. Zervas and I. Photaki, Chimica, 1960,14, 375.
5. G. Amiard, R. Heymes and L. Velluz, Bull. Soc. Chim., France,1956, 698.
6. M. Shinagawa, H. Nezu, H. Sunahara, F. Nakashima, O. Okashita and T. Yamada Proceedings of the 2nd International Congress on Advances Cambridge, England, 1960,**3**, 1142,
7. M. Brezina and V. Gultjaj , Collect. Ezech. Chem. Commun.,1963, **28**, 181.
8. V. Gultjaj,Collect. Ezech. Chem. Commun.,1959,**24**, 3046.
9. M.M. Taqui Khan, R.C. Bhardwaj and C. Bhardwaj,Inorg. Chim. Acta., 1987,**130**, 153.
10. V.M. Belousov, E.V. Kashuba and L.V. Lyashinko, Ukr. Khim, Zh. USSR., 1988, **54**, 1042.
11. R.C. Ogali and J. Walker ,Indian J. Chem.,1988,**27B**, 656.
12. X. D. Zhu, M. A. Nanny and E. C. Butter, J. Photochem. Photobiol., 2007,**185A,** 289.
13. M. I. Maldonado, P. C. Passarinho and I. Oller, J. Photochem. Photobiol.,2007, **185A,** 354.
14. S. Otsuka and M. Udea, J. Photochem. Photobiol., 2006,**8 A,** 1
15. A. Kiselev, A. Mattson and M. Andersson, J. Photochem. Photobiol., 2006,**184A,** 125.
16. Z. L. Liu, B. Guo, L. Hong and H. Jiang, J. Photochem. Photobiol., **172 A,** 81 (2005).
17. B. L. Yuan, Y. B. Li and X. D. Huang, J. Photochem. Photobiol.,).
18. S. Yamazaki, N. Yamabe and S. Nagano, J. Photochem. Photobiol., 2007, **185A,** 150.
19. H. Kominami, H. Sugahara and K. Hashimoto, *Catal. Commun*. 2010, **11** (5), 426.
20. H. Lv, L. Ma P. Zeng D. Ke and T. Peng *J. Mater. Chem.* 2010, **20** (18) 3665.
21. F. Spadavecchia, G. Cappelletti, S. Ardizzone, P. Scardi. (...),P. Fermo *Appl. Catal. B: Environmental, 2010*, **96** (3-4), 314.

22. J. M. Monteagudo, A. Durán, I. S. Martín and M. Aguirre, *Appl. Catal. B: Environmental, 2010*, **96** (3-4), 486.
23. C. C. Lo, C. W. Huang, C. H. Liao and J. C. S. Wu, *Inter. J. Hydrogen Energy*, 2010,**35** (4), 1523.
24. F. Chen, X. Yang, H. K. C. Mak and D. W. T. Chan, *Building Environment*, 2010, **45** (8), 1747.

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