Int. J. Chem. Sci. : 1 (2), 2003, 129–136

PHOTOCHEMICAL LIGAND EXCHANGE REACTIONS OF SODIUM NITROPRUSSIDE: USE OF BISULPHATE IONS

PIYUSH J. VYAS[a], SURESH G. PATEL[b] and PINKI B. PUNJABI*

Department of Chemistry,
Sukhadia University, Udaipur – 313002, (Raj.) INDIA

ABSTRACT

Sodium nitroprusside contains cyanide ligands that cannot be so easily replaced chemically. An effort has been made to substitute this ligand by another anionic ligand like bisulphate ion. The rate of this photochemical reaction has been observed spectrophotometrically. The effects of different parameters like pH, light intensity, concentration of sodium nitroprusside and bisulphate ligand on the rate of this substitution reaction have been studied. Product was isolated and characterized. A tentative mechanism for this photochemical substitution reaction has been proposed.

Keywords: Sodium nitroprusside, Sodium bisulphate, Photochemical substitution reaction.

INTRODUCTION

An aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light[1]. A number of workers have reported the photosensitivity of aqueous solution of nitroprusside in the nineteenth century, but unfortunately the results reported are contradictory with one another. It may be due to the probable failure to distinguish between primary photoreaction and secondary photochemical and/or thermal processes as well as to control the reaction conditions during irradiation. When aqueous[2] or acidic[3] solutions of the sodium nitroprusside were exposed to diffused day light, it was reported that nitric oxide was produced. Prussian blue was precipitated in this solution on long exposure. Mitra *et al.*[4] reported that initially a reversible reaction takes place on exposure of aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ with u.v. light. This reaction involves the production of a weak acid. On prolonged irradiation, secondary reactions occurred with the appearance of a dark blue colour and the reaction becomes irreversible from pH point of view. The dark blue colour was proposed to be due to the formation of some ferrous nitrites. Lal[5] observed that an aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ was converted into $[Fe(CN)_5(H_2O)]^{2-}$ on irradiation in the presence of hydrogen peroxide. A blue product was also reported, when this reaction was

---

[a] Department of Chemistry, Seth M.N. Science College, Patan–384265 (Gujarat) INDIA

[b] Department of Chemistry, H.N.S.B. Ltd. Science College, Himmatnagar–383001 (Gujarat) INDIA

carried out in the presence of thiourea[2] and thiocyanate[6], This blue product was proposed to be $[Fe(CN)_5(H_2O)]^{2-}$.

Van Voorst and Hemmerich[7] investigated the chemical reduction of nitroprusside solution in water and also in N, N – dimethylformamide and reported that the nature of reduced product depends on the acidity of the medium. The products have been tentatively assigned the structures as $[Fe(CN)_5(NO)]^{3-}$ or $[Fe(CN)_5(OH)]^{2-}$. The exchange reaction between $[Fe(CN)_5(NO)]^{2-}$ and CN^- ions is claimed to be photocatalysed[8]. The cyanide ligand trans to the NO group was reported to have a preferential exchange[9]. Reactions of thiourea with nitroprusside gave a red coloured adduct, which is gradually converted into a blue product[10]. Similar reaction was also shown by aqueous thiocyanate[11]. The formation of a hydroxo complex $[Fe(CN)_5(OH)]^{4-}$, NO_2^- and $[Fe(CN)_5(H_2O)]^{3-}$ has been reported by Sahasi[12] in photocatalytic reaction of sodium nitroprusside on some semiconducting oxides. Photochemical generation of nitroprusside induced by MLCT excitation in aqueous solution at room temperature was reported by Song and Lin[13]. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova *et al.*[14].

A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention. The photochemical reaction of sodium nitroprusside may be useful to have an insight in the understanding of its photochemical behaviour on one hand and it will also provide some alternate routes to prepare some newer complexes on the other. Recently, Mehta[15] studied photochemical reactions of nitroprusside in presence of some sulphur contatining ligands like sulphate, sulphite, thiosulphate etc.. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate (II), $[Fe(CN)_5(NO)]^{2-}$, in the presence of bisulphate ligands.

EXPERIMENTAL

Sodium nitroprusside (SNP) and sodium bisulphate were used in present investigation. 0.1 g and 0.04 g of sodium nitroprusside and sodium bisulphate were dissolved in 50 mL doubly distilled water, respectively and they were mixed in a 100 mL beaker. Then this solution was exposed to a 200 W tungsten lamp (Philips; light intensity = 13.0 $mWcm^{-2}$). The light intensity was measured with the help of a solarimeter (Suryamapi Model CEL 201). A water filter was used to cut off the thermal radiations. A digital pH meter (Systronics Model 324) was used to measure the pH of the solution. The desired pH of the solution was adjusted by the addition of previously standardized sulfuric acid or sodium hydroxide solutions.

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer (JASCO UV 7800). Estimation of Fe and Na in the products were made on atomic absorption spectrometer (Varian Techtron–AA–6D) and the estimation of carbon, hydrogen, nitrogen and sulfur were made on CARLO ERBA – 1106 microanalyser.

RESULTS AND DISCUSSION

An aliquot of 2.0 mL was taken out from the reaction mixture and the change in absorbance was observed at λ_{max} = 390 nm with time of exposure. It was observed that a plot of log (absorbance) Vs. time was linear and the rate constant of the reaction has been calculated by the expression –

$$k = 2.303 \times \text{slope} = 2.21 \times 10^{-4}\ \text{sec}^{-1}$$

The results are shown graphically in Figure 1.

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of bisulphate ligand may be affected by the pH values and, therefore, the effect of pH on this photochemical reaction has been investigated. The results are reported in Table 1.

Table 1. Effect of pH

[SNP] = 6.70×10^{-3}M [Bisulphate] = 6.63×10^{-3}M

Light Intensity = 50.0 mWcm^{-2}

pH	k x 10^4 (sec^{-1})
2.5	1.56
3.0	1.67
3.5	1.77
4.0	1.89
4.5	2.12
5.0	2.21
5.5	1.91
6.0	1.80

It was observed that the rate of this ligand exchange reaction increases on increasing the pH of the reaction medium. It reaches a maximum at pH = 5.0. A decrease in the rate of this reaction was observed on increasing pH further. It may be explained on the basis that as the pH was increased, the availability of the ligand ion HSO_4^- increases and hence, the reaction rate increases. But, on increasing the pH above 5.0, there is a possibility of a competitive reaction of ligand ions, HSO_4^- with that of OH^- ions. Thus, a corresponding decrease in the rate of reaction was observed.

Effect of Sodium Nitroprusside Concentration

The effect of the concentration of sodium nitroprusside on the rate of photochemical reaction was observed. The results are reported in Table 2.

Table 2. Effect of SNP concentration

pH = 5.0 [Bisulphate] = 6.63×10^{-3}M
Light Intensity = 50.0 mW. cm^{-2}

[SNP] x 10^3 M	k x 10^4 (sec^{-1})
3.3	1.81
4.0	1.96
4.6	2.02
5.3	2.10
6.0	2.21
6.7	2.36
7.3	2.19
8.0	1.89
8.7	1.77

It has been observed that the rate of photochemical reaction of sodium nitroprusside with bisulphate ions increases with an increase in the concentration of sodium nitroprusside. This may be due to the fact that as the concentration of sodium nitroprusside was increased, the number of excited species also increase; thus, resulting into a corresponding increase in the rate of reaction. After a certain limit, if the concentration of sodium nitroprusside was further increased, there was a decrease in the rate of the reaction. This decrease may be explained on the basis that the substrate is dark red coloured, which will absorb a major part of incident radiation travelling through the reaction mixture and, therefore, there will be a decrease in the light intensity reaching sodium nitroprusside in the bulk of reaction mixture. In other words, the solution of nitroprusside will start acting as a filter and as a consequence, the reaction rate was found to decrease.

Effect of Bisulphate Concentration

The effect of concentration of bisulphate on the rate of photochemical reaction of sodium nitroprusside was also observed by taking different concentration of bisulphate. The results are summarized in Table 3.

Table 3. Effect of bisulphate ion concentration

[SNP] = 6.70 x 10^{-3} M pH = 5.0

Intensity of Light = 50.0 mw cm^{-2}

[Bisulphate] x 10^3 M	k x 10^4 (sec^{-1})
2.21	1.53
3.32	1.55
4.42	1.78
5.53	1.91
6.63	2.21
7.74	2.05
8.84	1.91
9.97	1.75

It was observed that as the concentration of sodium bisulphate was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [$NaHSO_4$] = 6.63 x 10^{-3} M. It can be explained on the basis of the fact that the reaction rate increases due to increase in the concentration of participating species. On the other hand, a decrease in the rate of the reaction was observed on increasing the concentration of sodium bisulphate above 6.63 x 10^{-3} M. It may be attributed to the fact that higher concentrations of bisulphate ions may hinder its own movement to reach the excited species of sodium nitroprusside in a desired time limit. Thus, a decrease in the rate of the reaction was observed for higher concentrations of bisulphate ions.

Effect of Light Intensity

The effect of intensity of light on the rate of photochemical reaction of sodium nitroprusside has been observed by varying the distance between the exposed surface of the reaction mixture and the source. The results are tabulated in Table 4.

Table 4. Effect of light intensity

[SNP] = 6.70×10^{-3} M [Bisulphate] = 6.63×10^{-3}M

pH = 5.0

Intensity of light ($mWcm^{-2}$)	k x 10^4 (sec^{-1})
10.0	1.11
15.0	1.24
20.0	1.55
25.0	1.66
30.0	1.70
35.0	1.78
40.0	1.91
45.0	2.07
50.0	2.21
55.0	2.21
60.0	2.21

The results indicate that reaction rate is accelerated as the intensity of light was increased. This may be due to the fact that any increase in the light intensity will increase the number of photons striking per unit area of the reaction mixture. After a certain limit i.e., I = 50.0 $mWcm^{-2}$, no reasonable increase in the rate of reaction has been observed. Rather, it reaches a saturation point at a particular intensity. It suggests that further increase in the light intensity will not increase the rate of this photochemical reaction any more, as the surface of the reaction mixture remains fixed.

An effort was made to know the requirement of light in different steps of this reaction. It was observed that the reaction stops at a particular step, as soon as the light source was cut off. The reaction reaches its completion only, when the light exposure was continued throughout the progress of the reaction.

PRODUCT ANALYSIS

In neutral medium, the photochemical reaction between nitroprusside and bisulphate was carried out. It was observed that the initial light red colour of the reaction mixture changes to dark green. The reaction was allowed to proceed to completion and then it was filtered. The filtrate was evaporated on a water bath and the residue was recrystallised with methanol giving dark green crystals of the product, which was analysed as follows :

(i) Elemental Analysis :

Found $Fe = 11.08\ \%, C = 7.2\ \%, H = 1.0\ \%,$
$N = 8.10\%, S = 18.00\ \%$ and $Na = 18.00\ \%$

Calculated $Fe = 11.0\ \%, C = 6.94\ \%, H = 0.57\ \%,$
$N = 8.10\%, S = 18.53\ \%$ and $Na = 17.76\%$

(ii) u.v. (water): $\lambda_{max} = 413$ nm and 519 nm

(iii) i.r. $\nu_{(KBr)}$: A comparison of the i.r. spectra of the sodium nitroprusside, sodium bisulphate and the product clearly indicates the removal of nitrosyl ligand from the coordination sphere of the iron. The characteristic bands of NO^+ ligand at 1944 and 660 cm^{-1} were found absent in the i.r. spectrum of the product. It is known that bisulphate ion has characteristic bands at 1160, 1040, 860 and 840 cm^{-1}. It was observed that bands at 1160 and 845 cm^{-1} also appeared in the i.r. spectrum of the product. These bands may be attributed to the presence of M–O bonded bisulphate ligand to the central metal ion.

The test of CN^- ions was found positive in solution. On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound.

$$Na_4\,[Fe(CN)_3\,(HSO_4)_3]$$

In this case, bisulphate behaves as a unidentate ligand. Three bisulphate ions have been used for replacing two CN^- and one NO^+ ligand from the coordination sphere of the iron.

MECHANISM

On the basis of the experimental observations, a tentative mechanism for this photochemical ligand exchange reaction of sodium nitroprusside has been proposed as :

$$Na_2\,[Fe(CN)_5NO] \xrightarrow{h\nu} Na_2[Fe(CN)_5NO]^{*+} + e^-$$

$$Na_2[Fe(CN)_5NO]^{*+} + H_2O \xrightarrow{h\nu} Na_3[Fe(CN)_5(H_2O)] + NO^+$$

$$Na_3[Fe(CN)_5(H_2O) + HSO_4^- \longrightarrow Na_4[Fe(CN)_5(HSO_4)] + H_2O$$

$$Na_4[Fe(CN)_5(HSO_4)] + 2HSO_4^- \longrightarrow Na_4[Fe(CN)_3(HSO_4)_3] + 2\,CN^-$$

Initially, the sodium nitroprusside is excited by absorbing incident radiations of desired wavelength. Then its excited state will react with water and as a consequence, water enters the coordinations sphere of iron, replacing nitrosylium ion (NO^+). This exchange is energetically favourable, because neutral ligand (H_2O), can replace cationic ligand (NO^+). Now bisulphate ions can easily throw water molecules out of the coordination sphere of iron as anionic ligand can replace a neutral ligand. In the last step, another two bisulphate ions (a weaker ligand) push two cyanide ions (a stronger ligand) as evident for the chemical analysis of the product.

These ligand exchange reactions are well known in the field of coordination chemistry, but these reactions ordinarily involve the substitution of a weaker ligand by a stronger ligand. Such reactions are both, thermodynamically and kinetically, favourable. It does not seem feasible to have reverse exchange i.e. substituting a stronger ligand by a weaker ligand. The present work not only provides a pathway for this unfavourable reaction, but it will also open further avenues for such photochemical ligand exchange reactions.

ACKNOWLEDGMENT

The authors are grateful to R & D Department, IFFCO, Kalol (North Gujarat) for estimation of Fe and Na and Meta Research Laboratories, Ahmedabad for elemental analysis.

REFERENCES

1. J. F. Swinehast, *Coord. Chem. Revs.*, **2**, 385 (1967).
2. O. Baudisch, *Science*, **108**, 443 (1948).
3. E. Justin–Mueller, *Bull. Soc. Chim.*, **2**, 1932 (1935).
4. R. P. Mitra, C. V. S. Jain, A. K. Banerjee and K. V. R. Chari, *J. Inorg. Nucl. Chem.*, **25**, 1263 (1963).
5. B. B. Lal, *Proc. Indian Acad. Sci.*, **A–14**, 652 (1941).
6. N. Tarugi, *Ann. Chim. Appl.*, **16**, 407 (1926).
7. J. D. W. Van Voorst and P. Hemmerich , *J. Chem. Phys.*, **45**, 3914 (1966).
8. W. Adamson and A. H. Sporer , *J. Amer. Chem. Soc.*, **80**, 3865 (1958).
9. J. H. Swinehart and P. A. Rock , *Inorg. Chem.*, **5**, 573 (1966).
10. P. A. Stoeri and D. X. West , *J. Inorg. Nucl. Chem.*, **36** (1974) 3883.
11. J. A. Mecleverty, *Chem. Revs.*, **79**, 53 (1979).
12. S. Sahasi, *Ph.D. Thesis,* Sukhadia University, Udaipur, India, (1991).
13. Q. H. Song and Q. Z. Lin , *J. Photochem. Photobiol.*, **114A**, 181 (1998).
14. L. A. Anisimova, I. A. Yushenko and V. F. Toropova, *J. Anal. Chem.*, **52**, 1049 (1997).
15. M. R. Mehta, *Ph.D. Thesis,* Sukhadia University, Udaipur, India, (2001).

Accepted 10.5.2003