Asian Journal of Chemistry Vol. 15, No. 1 (2003), 287–294

Photochemical Reactions of Sodium Nitroprusside in Presence of Bicarbonate Ions

PIYUSH J. VYAS, MUKESH MEHTA and PINKI B. PUNJABI*
Department of Chemistry, College of Science, Sukhadia University, Udaipur-313 002, India

Cyanide ligand (a strong ligand) present in sodium nitroprusside is not so easily replaced chemically. An effort has been made to replace this ligand by another anionic ligand like bicarbonate (a weak ligand). The rate of this photochemical exchange reaction has been observed spectrophotometrically. The effects of different parameters like pH, light intensity, concentration of sodium nitroprusside and bicarbonate ligand concentration on the rate of this substitution reaction have been studied. An effort was made to isolate the product and characterize it. A tentative mechanism for this photochemical substitution reaction has been proposed.

Key Words: Sodium nitroprusside, Sodium bicarbonate, Photochemical substitution reaction.

INTRODUCTION

In the presence of light an aqueous solution of sodium nitroprusside undergoes a complex decomposition process[1]. The photosensitivity of aqueous solution of nitroprusside in the nineteenth century was reported by a number of workers, 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 sodium nitroprusside were exposed to diffused daylight, it was reported that nitric oxide was produced. Prussian blue was precipitated in this solution on long exposure. Lal[4] 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 the same reaction was carried out in the presence of thiourea[2] and thiocyanate[5]. This blue product was proposed to be $[Fe(CN)_5(H_2O)]^{2-}$. When an aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ was exposed to UV light, initially a reversible reaction took place[6]. This reaction involves the production of a weak acid. On prolonged irradiation, secondary reactions occur with the appearance of a dark blue colour and the reaction becomes irreversible from pH point of view. The dark blue colour is proposed to be due to the formation of some ferrous nitrites.

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 fornation 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. Similar photocatalysed reaction involving nitroprusside-thiocyanate system was reported by Dak *et al.*[13]. Song and Lin[14] investigated the photochemical generation of nitroprusside induced by MLCT excitation in aqueous solution at room temperature. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova *et al.*[15]

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 into 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[16] studied the photochemical reactions of sodium nitroprusside in the presence of some sulphur containing ligands. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate(II), $[Fe(CN)_5(NO)]^{2-}$, in the presence of bicarbonate ligand.

EXPERIMENTAL

Sodium nitroprusside (EM) and sodium bicarbonate (SDS) were used in the present investigation. 0.18 g and 0.12 g of sodium nitroprusside and sodium bicarbonate were dissolved in 100 mL doubly distilled water. Then this solution was exposed to a 200 W tungsten lamp (Philips, light intensity = 80.0 mW cm^{-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) measured the pH of the solution. The desired pH of the solution was adjusted by the addition of previously standardized sulfuric acid and sodium hydroxide solutions.

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer (JASCO UV 7800). Estimations of Fe and Na in the products were made on atomic absorption spectrometer (Varian Techtron-AA-6D) and the estimations 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 $\lambda_{max} = 390$ nm with time of exposure. It was observed that a plot of log (absorbance) *vs.* time was linear and it followed pseudo-first order kinetics. The rate constant of the reaction has been calculated by the expression

$$k = 2.303 \times \text{slope}.$$

The results are graphically shown in Fig. 1.

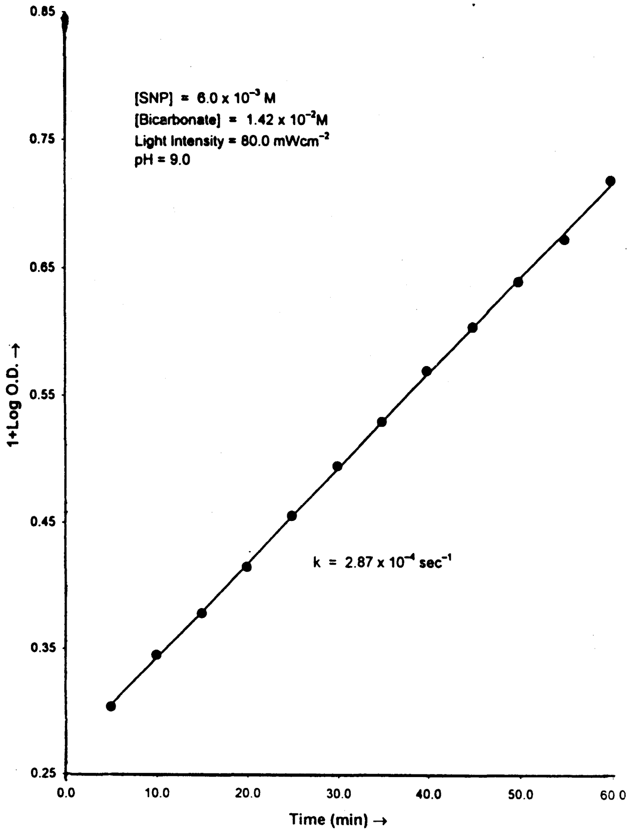

Fig. 1. A Typical Run.

Effect of pH: The photochemical reaction of sodium nitroprusside (SNP) in presence of bicarbonate 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] = 6.0×10^{-3} M; [Bicarbonate] = 1.42×10^{-2} M; Light intensity = 80.0 mW cm^{-2}

pH	$k \times 10^4$ (sec^{-1})
6.5	1.59
7.0	1.98
7.5	2.11
8.0	2.17
8.5	2.23
9.0	2.87

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 = 9.0. This may be explained on the basis that as the pH of the medium was increased, the extent of availability of HCO_3^- ions to remain in its best donor form will increase, which will result into a corresponding increase in the rate of ligand exchange reaction. It was not possible to observe the effect of pH on the rate of the reacticm above pH 9.0 due to the fact that a chemical reaction starts interfering with the main photochemical reaction. It was not possible to observe this reaction in the acidic range because the bicarbonate ions exist as carbonic acid, which is unstable and therefore decomposes to carbon dioxide and water.

Effect of sodium nitroprusside concentration: The effect of the concentration of sodium nitroprusside on the rate of photochemical reaction was observed by keeping all other factors identical. The results are reported in Table-2.

TABLE-2
EFFECT OF SODIUM NITROPRUSSIDE CONCENTRATION

pH = 9.0; [Bicarbonate] = 1.42×10^{-2} M; Light Intensity = 80.0 mW cm^{-2}

[Sodium nitroprusside] $\times 10^3$ M	$k \times 10^4$(sec^{-1})
4.0	1.53
4.6	2.01
5.3	2.49
6.0	2.87
6.7	2.68
7.3	2.22
8.0	2.01
8.7	1.85

It has been observed that the rate of photochemical reaction of sodium nitroprusside with bicarbonate 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 increased, 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 the reaction mixture. In other words, the solution of sodium nitroprusside will start acting as a filter and, as a consequence, the reaction rate will be found to decrease.

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

TABLE-3
EFFECT OF BICARBONATE CONCENTRATION

[SNP] = 6.0×10^{-3} M; pH = 9.0; Intensity of light = 80.0 mW cm^{-2}

[Bicarbonate] × 10^3 M	k × 10^4 (sec^{-1})
0.95	2.49
1.19	2.59
1.42	2.87
1.66	2.57
1.90	2.11
2.10	1.91
2.30	1.77

It was observed that as the concentration of sodium bicarbonate was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [$NaHCO_3$] = 1.42×10^{-2} 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 bicarbonate above 1.42×10^{-2} M. It may be attributed to the fact that higher concentrations of bicarbonate 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 bicarbonate 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] = 6.0×10^{-3} M; [Bicarbonate] = 1.42×10^{-2} M; pH = 9.0

Intensity of light (mW cm^{-2})	$k \times 10^4$ (sec^{-1})
10.0	1.40
20.0	1.43
30.0	1.53
40.0	2.04
50.0	2.14
60.0	2.21
70.0	2.67
80.0	2.87
90.0	2.87
100.0	2.87

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 of the reaction mixture. After a certain limit, *i.e.*, I = 80.0 mW cm^{-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 stopped at a particular step, as soon as the light source was cut off. The reaction reached its completion only, when the light exposure was continued throughout the progress of the reaction.

Product analysis: In alkaline medium, it was observed that the initial light red coloured solution of the reaction mixture changes to dark yellow (red shade) on irradiation. The reaction was allowed to proceed to completion and the reaction mixture was then filtered. The filtrate was evaporated on a water bath. The product was separated by fractional crystallisation. It was recrystallized with methanol giving reddish yellow crystals of the product, which was analysed as follows:

(i) Elemental Analysis (%): Found Fe = 16.7, C = 19.9, H = 1.0, N = 2058 and Na = 28.00 Calculated: Fe = 16.76, C = 21.17, H = 0.92, N = 20.58 and Na = 27.05.

(ii) UV (water): λ_{max}= 460 nm

(iii) IR ν_{KBr}: The characteristic bands of NO^+ ligand at 1944 and 660 cm^{-1} were found absent in the IR spectrum of the product and therefore it may be concluded that nitrosyl ligand has been lost during this photochemical reaction. It has been observed that the bicarbonate ion has characteristic bands at 985, 835 and 700 cm^{-1}. It was observed that bands at 980, 860 and 700 cm^{-1} also appeared in the IR spectrum of the product. These bands may be attributed to the presence of O-bonded bicarbonate ligand to the central metal ion.

On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound: $Na_4[Fe(CN)_5(HCO_3)]$.

In this case bicarbonate behaves as a unidentate ligand used for removing one NO^+ ligand from the coordination sphere of the sodium nitroprusside complex. A positive test for nitrite ion in the solution has been observed which indicates the removal of NO^+.

Mechanism

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

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

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

$$Na_3[Fe(CN)_5(H_2O)] + HCO_3^- \longrightarrow Na_4[Fe(CN)_5(HCO_3)] + H_2O$$

Initially, the sodium nitroprusside is excited by absorbing incident radiations of desired wavelength. Then its excited state reacts with water and as a consequence, water enters the coordination sphere of iron, replacing nitrosylium ion (NO^+). This exchange is energetically favourable, because neutral ligand (H_2O) can replace cationic ligand (NO^+). Now bicarbonate ions can easily throw water molecules out of the coordination sphere of iron as anionic ligand can replace a neutral ligand.

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 also it will open further avenues for such photochemical ligand exchange reactions.

ANKNOWLEDGEMENTS

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

REFERENCES

1. J.F. Swinehart, *Coord. Chem. Rev.*, **2**, 385 (1967).
2. O. Baudisch, *Science*, **108**, 443 (1948).
3. E. Justin-Mueller, *Bull. Soc. Chim.*, **2**, 1932 (1935).
4. B.B. Lal, *Proc. Indian Acad. Sci.*, **14A**, 652 (1941).
5. N. Tarugi, *Ann. Chim. Appl.*, **16**, 407 (1926).
6. R.P. Mitra, C.V.S. Jain, A.K. Banerjee and K.V.R. Chari, *J. Inorg. Nucl. Chem.*, **25**, 1263 (1963).
7. J.D.W. Van Voorstand and P. Hemmerich, *J. Chem. Phys.*, **45**, 3914 (1966).
8. W. Adamson and A.H. Sporer, *J. Am. 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**, 3883 (1974).
11. J.A. Mecleverty, *Chem. Revs.*, **79**, 53 (1979).
12. S. Sahasi, Ph.D. Thesis, Sukhadia University, Udaipur, India (1991).
13. M. Dak, B. Sharma, M. Mehta and S.C. Ameta, *Izv. Vys. Vchne Zave Khimiya I*, **37**, 43 (1994).
14. Q.H. Song and Q.Z. Lin, *J. Photochem. Photobiol.*, **114A**, 181 (1998).
15. L.A. Anisimova, I.A. Yushenko and V.F. Toropova, *J. Anal. Chem.*, **52**, 1049 (1997).
16. M.R. Mehta, Ph.D. Thesis, Sukhadia University, Udaipur, India (2001).

(*Received*: 25 June 2002; *Accepted:* 21 August 2002) AJC-2832