LIGAND EXCHANGE REACTION OF SODIUM NITROPRUSSIDE IN THE PRESENCE OF CARBONATE IONS UNDER PHOTOCHEMICAL CONDITIONS

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ABSTRACT

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 carbonate (a weak ligand). The rate of this photochemical exchange reaction has been observed spectrophotometrically. The effect of different parameters like pH, light intensity, concentration of sodium nitroprusside and carbonate 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 carbonate, Photochemical substitution.

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 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 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. Lal[4] observed that an aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ was converted into $[Fe(CN)_5(H_2O)]^{2-}$. When aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ was exposed with u.v. light; initially, a reversible reaction takes place[6]. 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.

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. Similar photocatalysed reaction involving nitroprusside–thiocyanate system was reported by Dak *et al.*[13]. Sone 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 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[16] studied the photochemical reactions of sodium nitroprusside in the presence of some sulphur containing ligands. Carbonate ion coordinate with a metal as a unidentate or a bidentate ligand. In the free ion, all the C–O bonds are equivalent. When it coordinates with a metal atom, there are now two types of bonds. But this difference between the two kinds of C–O bonds will be much greater in those complexes, where $CO_3 2-$ ion acts as a bidentate ligand than as a unidentate ligand. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate (II), $[Fe(CN)_5(NO)]^{2-}$, in the presence of carbonate ligand.

EXPERIMENTAL

Sodium nitroprusside (EM) and sodium carbonate (SC) were used in present investigation. 0.20 g of sodium nitroprusside and 0.10 g of sodium carbonate were dissolved in 100 mL doubly distilled water and was exposed to a 200 W tungsten lamp (Philips; light intensity = 50.0 $mWcm^{-2}$). 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 and 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) v/s time was linear and it followed pseudo – first order kinetics. The rate constant of the reaction has been calculated by the expression

$$k = 2.303 \times slope.$$

The results are graphically shown in Figure 1.

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of carbonate 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.

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 = 10.0. This may be explained on the basis that as the pH of the medium was increased the extent of availability of CO_3^{2-} ions to remain in its best donor form will increase, which will result into a corresponding increase in the rate of ligand exchange reaction.

Table 1
Effect of pH

[SNP] = 6.70 x 10^{-3} M   [Sodium carbonate] = 9.43 x 10^{-3} M

Light Intensity = 50.0 mWcm^{-2}

pH	k x 10^4 (sec^{-1})
6.5	1.69
7.0	1.90
7.5	1.91
8.0	2.17
8.5	2.30
9.0	2.39
9.5	2.74
10.0	3.99

It was not possible to observe the effect of pH on the rate of reaction above pH 10.0 due to the fact that a chemical reaction starts interfering the main photochemical reaction. It was not possible to observe this reaction in acidic range because the carbonate ions exists 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. The results are reported in Table 2.

It has been observed that the rate of photochemical reaction of sodium nitroprusside with carbonate ions in-

[SNP] = 6.7×10^{-3} M
[Sodium carbonate] = 9.43×10^{-3} M
pH = 10.0
Light Intensity = 50.0 mWcm^{-2}

$k = 3.99 \times 10^{-5}$ sec^{-1}

1 + Log O.D. →

Time (min) →

Figure 1 : A Typical Run

creases 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.

Table 2
EFFECT OF SNP CONCENTRATION

pH = 10.0   [Sodium carbonate] = 9.43×10^{-3} M

Light intensity = 50.0 mWcm^{-2}

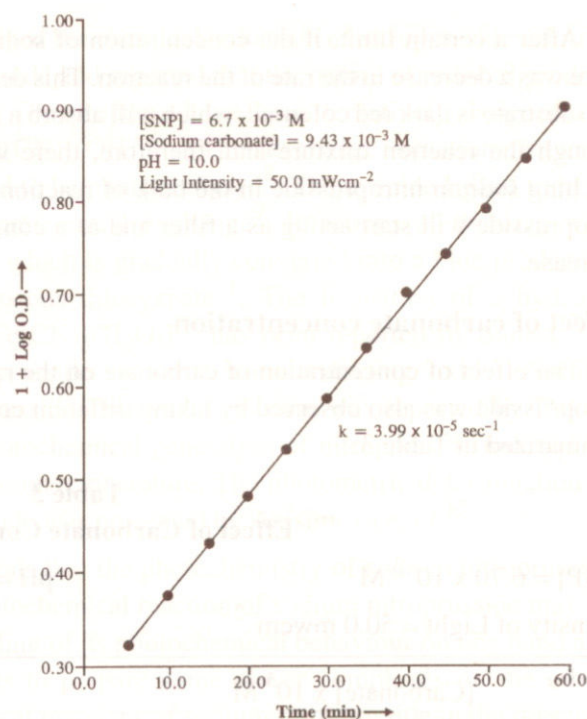| Sodium nitroprusside x 10^3 M	k x 10^4 (sec^{-1})
4.0	2.21
4.6	3.10
5.3	3.67
6.0	3.83
6.7	3.99
7.3	3.67
8.0	3.24
8.7	3.19

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 carbonate concentration

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

Table 3
Effect of Carbonate Concentration

[SNP] = 6.70×10^{-3} M   pH = 10.0

Intensity of Light = 50.0 mwcm^{-2}

[Carbonate] x 10^3 M	k x 10^4 (sec^{-1})
1.88	2.95
3.77	3.35
5.66	3.51
7.54	3.83
9.43	3.99
11.30	3.69
13.20	3.54
15.00	3.51

It was observed that as the concentration of sodium carbonate was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [Na$_2$CO$_3$] = 9.43×10^{-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 carbonate above 9.43×10^{-3}M. It may be attributed to the fact that higher concentrations of carbonate 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 carbonate 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

$[SNP] = 6.70 \times 10^{-3}$ M $[Sodium\ carbonate] = 9.43 \times 10^{-3}$ M

pH = 10.0

Intensity of Light (mWcm^{-2})	$k \times 10^4$ (sec^{-1})
10.0	2.21
20.0	2.39
30.0	2.87
40.0	3.69
50.0	3.99
60.0	3.99
70.0	3.99
80.0	3.99

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 increases 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 through out the progress of the reaction.

Product Analysis

In alkaline medium, it was observed that the initial light red colour of the reaction mixture turned dark yellow 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 recrystallised with methanol giving green crystals of the product, which was analysed as follows –

(i)   Elemental Analysis :

Found Fe = 14.0 %, C = 14.03%, N = 13.30%, Na = 30.90%

Calculated Fe = 13.60%, C = 14.31%, N = 13.36%, and Na = 32.93%

(ii) u.v. (water) – $\lambda_{max} = 410$ nm

(iii) i.r. – A comparison of the i.r. spectra of the sodium nitroprusside and the product reveals that two bands present at 1944 and 660 cm^{-1} in the i.r. spectrum of nitroprusside were found absent in the i.r. spectrum of the product. Absence of these bands may be attributed to the removal of NO$^+$ and CN$^-$ ligands from the coordination sphere of the central metal ion. It has been observed that carbonate ion has characteristic bands at 1320, 1050, 855 and 740 cm^{-1}. It was observed that bands at 1320, 1050, 855 and 720 cm^{-1} also appeared in the i.r. spectrum of the product. These bands may be attributed to the presence of O–bonded carbonate ligand to the central metal ion (Iron).
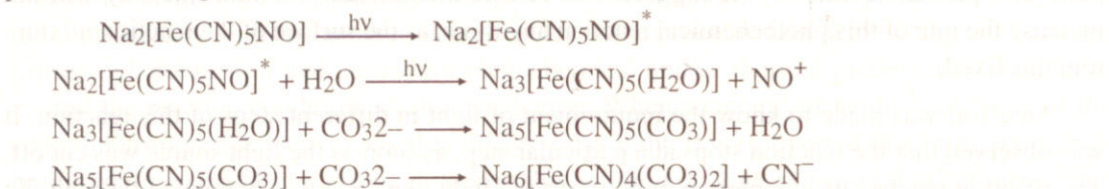
On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound.

$$Na_6[Fe(CN)_4(CO_3)_2]$$

In this case carbonate behaves as a unidentate ligand. Two carbonate ions have been used for replacing one CN$^-$ and one NO$^+$ ligand from the coordination sphere of the sodium nitroprusside complex. A positive test for nitrite ion in the solution has also 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 –

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

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

$$Na_3[Fe(CN)_5(H_2O)] + CO_3{2-} \longrightarrow Na_5[Fe(CN)_5(CO_3)] + H_2O$$

$$Na_5[Fe(CN)_5(CO_3)] + CO_3{2-} \longrightarrow Na_6[Fe(CN)_4(CO_3)_2] + CN^-$$

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$_2$O), can replace cationic ligand (NO$^+$). Now carbonate 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 carbonate ion (a weaker ligand) push cyanide ion (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.

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