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Photochemical Ligand Exchange Reactions of Sodium Nitroprusside: Use of Metabisulphite Ions

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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 metabisulphite. The rate of this photochemical reaction has been observed spectrophotometrically. The effect of different parameters like pH, light intensity, concentration of sodium nitroprusside and metabisulphite ligand concentration on the rate of this substitution reaction have been studied. The product has beem isolated and characterized. A tentative mechanism for this photochemical substitution reaction has been proposed.

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

INTRODUCTION

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 reaction conditions during irradiation. When aqueous[2] or acidic[3] solutions of the 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. Mitra *et al.*[4] reported that initially a reversible reaction takes place on exposure of aqueous solution of $[Fe(CN)_5(NO)]^{2-}$ with UV light. 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 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 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[15]. 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. The present work describes the photochemical reaction of pentacyanonitrosyl ferrate(II), $[Fe(CN)_5(NO)]^{2-}$, in the presence of metabisulphite ligands.

EXPERIMENTAL

Sodium nitroprusside (EM) and sodium metabisulphite (SDS) were used in the present investigation. 0.3586 g of sodium nitroprusside and 0.1498 g of sodium metabisulphite ($S_2O_5^{2-}$) were dissolved in 100 mL doubly distilled water and was exposed to a 200 W tungsten lamp (Philips; light intensity = 14.0 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). Estimation of Fe and Na in the products was made on atomic absorption spectrometer (Varian Techtron-AA-6D) and the estimation of carbon, hydrogen, nitrogen and sulfur was made on Carlo Erba-1106 microanalyser.

RESULTS AND DISCUSSION

An aliquot of 5.0 mL was taken out from the reaction mixture and the change in absorbance was observed at $\lambda_{max} = 620$ 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.

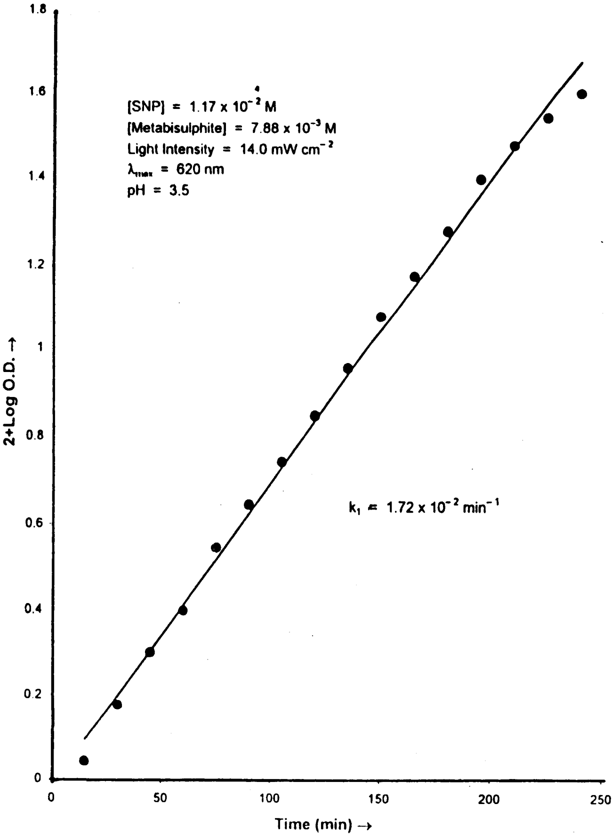

Fig. 1. A Typical Run.

Effect of pH: The photochemical reaction of sodium nitroprusside in pesence of metabisulphite 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 = 3.5. 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 increased in its anionic form $S_2O_5^{2-}$ and, hence, the reaction rate increases. But, on increasing the pH above 3.5, there is a possibility of a competitive reaction of ligand ions, $S_2O_5^{2-}$ with that of OH^- ions. Thus, a corresponding decrease in the rate of reaction was observed.

TABLE-1
EFFECT OF pH

[SNP] = 1.17×10^{-2} M, [Metabisulphite] = 7.88×10^{-3} M, Light intensity = 14.0 mW cm^{-2}

pH	$k \times 10^2$ (min^{-1})
2.0	1.15
2.5	1.32
3.0	1.54
3.5	1.72
4.0	1.54
4.5	1.45
5.0	1.31
5.5	1.20
6.0	1.10
7.0	1.00
8.0	0.91

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 SODIUM NITROPRUSSIDE CONCENTRATION

[Metabisulphite] = 7.88×10^{-3} M, Light Intensity = 14.0 mW cm^{-2}, pH = 3.5

[Sodium nitroprusside] $\times 10^2$ M	$k \times 10^2$ (min^{-1})
1.04	1.17
1.07	1.24
1.09	1.33
1.10	1.38
1.12	1.47
1.14	1.54
1.15	1.60
1.17	1.72
1.21	1.59
1.22	1.52
1.23	1.43
1.24	1.34
1.26	1.27
1.28	1.20

It has been observed that the rate of photochemical reaction of sodium nitroprusside with metabisulphite 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 is increased, the number of excited species also increases, thus resulting into a corresponding increase in the rate of reaction. After a certain limit, if the concentration of sodium nitroprusside is further increased, there is 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 is found to decrease.

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

TABLE-3

EFFECT OF METABISULPHITE CONCENTRATION

[SNP] = 1.17×10^{-2} M, Light Intensity = 14.0 mW cm^{-2}, pH = 3.5

[Metabisulphite] $\times 10^3$ M	k $\times 10^2$ (min^{-1})
6.31	1.27
6.50	1.34
6.84	1.45
7.10	1.51
7.36	1.57
7.61	1.64
7.88	1.72
8.20	1.61
8.42	1.54
8.70	1.48
8.94	1.43
9.30	1.36
9.47	1.29

It was observed that as the concentration of sodium metabisulphite was increased, there was a corresponding increase in the rate of reaction, reaching a maximum at [$Na_2S_2O_5$] = 7.88×10^{-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 metabisulphite above 7.88×10^{-3} M.

It may be attributed to the fact that higher concentrations of metabisulphite 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 metabisulphite 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. The results indicate that reaction rate is accelerated as the intensity of light is 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 = 14.0 mW cm^{-2}, no reasonable increase in the rate of reaction is 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.

TABLE-4
EFFECT OF LIGHT INTENSITY

[SNP] = 1.17×10^{-2} M, [Metabisulphite] = 7.88×10^{-3} M, pH = 3.5

Intensity of light (mW cm^{-2})	$k \times 10^2$ (min^{-1})
6.0	1.27
7.0	1.32
8.0	1.36
9.0	1.41
10.0	1.45
11.0	1.50
12.0	1.54
13.0	1.63
14.0	1.72
16.0	1.72
20.0	1.72

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 reaches its completion only when the light exposure was continued throughout the progress of the reaction.

Analysis of the product: In neutral medium, the photochemical reaction between nitroprusside and metabisulphite was carried out. It was observed that the initial light red colour of the reaction mixture changes to peacock blue. 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 green crystals of the product, which was analysed as follows:

(i) Elemental Analysis (%): Found: Fe = 13.00, C = 13.32, N = 15.50, S = 14.54 and Na = 25.50. Calculated: Fe = 12.78, C = 13.54, N = 15.69, S = 14.34, and Na = 25.78.

(ii) UV (water): λ_{max} = 480 nm.

(iii) IR ν(KBr): A comparison of the IR spectra of sodium nitroprusside, sodium metabisulphite and the product clearly indicates the removal of nitrosyl ligand from the coordination sphere of iron. The characteristic bands of NO^+ ligand at 1944 and 670 cm^{-1} were found absent in the IR spectrum of the product. It is known that metabisulphite ion has characteristic bands at 1050 and 990 cm^{-1}. It was observed that bands at 1090 and 980 cm^{-1} also appeared in the IR spectrum of the product. These bands may be attributed to the presence of O-bonded metabisulphite ligand to the central metal ion.

The test of CN^- ions was found negative in solution. On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound. $Na_5[Fe(CN)_5(S_2O_5)]$.

In this case metabisulphite behaves as a unidentate ligand. One metabisulphite ion has been used for removing NO^+ ligand from the coordination sphere of the sodium nitroprusside complex. A positive test for the 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:

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

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

$$Na_3[Fe(CN)_5(H_2O)] + S_2O_5^{2-} \xrightarrow{h\nu} Na_5[Fe(CN)_5(S_2O_5)] + H_2O$$

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 coordination sphere of iron, replacing nitrosylium ion (NO^+). This exchange is energetically favourable, because neutral ligand (H_2O) can replace cationic ligand (NO^+). Now metabisulphite 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.

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