

STUDY OF PHOTOCHEMICAL REACTION INVOLVING NITROSYL PENTACYANOFERRATE (II): DIMETHYLUREA SYSTEM

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ABSTRACT

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

Key words: Sodium nitroprusside, Dimethylurea, Photochemical substitution reaction.

INTRODUCTION

Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light¹. Van Voorst and Hemmerich² 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 exchange reaction between $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and CN ions is claimed to be photocatalysed³. The cyanide ligand, trans to the NO group was reported to have a preferential exchange⁴. Reactions of thiourea with nitroprusside gave a red colored adduct, which is gradually converted into a blue product⁵. The formation of a hydroxo complex $[\text{Fe}(\text{CN})_5(\text{OH})]^{4-}$, NO_2 and $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ has been reported by Sahasi⁶ 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 Lin⁷. The photometric determination of thiourea with the use of sodium nitroprusside was presented by Anisimova et al.⁸ A critical survey of the literature reveals that the photochemistry of sodium nitroprusside has received negligible attention. The photochemical ligand exchange reactions of sodium nitroprusside have been reported by Ameta et al.⁹ and Prajapati et al.¹⁰ Photolytic decomposition was studied by Singh et al.¹¹ The photochemical substitution reaction of nitrosyl pentacyanoferrate (II) with Br and I were observed by Chauhan et al.^{12,13} The photochemical reaction of sodium nitroprusside may be useful to have an insight in the understanding of its photochemical behavior on one hand and it will also provide some alternate route to prepare some complexes on the other. The present work describes the photochemical reaction of pentacyanonitrosylferrate (II), $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$, in the presence of ligand like dimethylurea.

EXPERIMENTAL

In present study, 0.3232 g of sodium nitroprusside and 0.01665 g of dimethylurea were dissolved in 50.0 mL of distilled water and these was mixed in a 100.0 mL beaker. Then this solution was exposed to a 200 W tungsten lamp (Philips, light intensity = 21.0 mWcm⁻¹). The light intensity was measured with the help of a solarimeter (Suryamapi model CEL 201). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer (Systronics model 106). Estimation of Fe and Na in the products was made on atomic absorption spectrometer, AAS (Model Varian Techtron-AA-6D) and the estimation of carbon, hydrogen and nitrogen were made on Carlo-Erba-1106 micro analyzer at Sophisticated Instrumentation Centre for Applied Research & Testing, SICART, Vallabh Vidyanagar, Gujarat.

RESULTS AND DISCUSSION

An aliquot of 5.0 mL was taken out from the reaction mixture and the change in optical density was observed colorimetrically at $\lambda_{\max} = 620$ nm with time of exposure. It was observed that a plot of log (optical density) v/s time was linear and it followed pseudo-first order kinetics. The rate constant of the reaction has been calculated by the expression.

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

The results are summarized in Table 1 and graphically shown in Fig. 1.

Table 1: A typical run

[SNP] = 1.08 x 10⁻² M [Dimethylurea] = 1.89 x 10⁻³ M
 pH = 3.8 Light intensity = 21.0 mWcm⁻²
 $\lambda_{\max} = 620$ nm

Time (min.)	O.D.	2 + log O.D.
10.0	0.051	0.7076
20.0	0.059	0.7709
30.0	0.081	0.9085
40.0	0.108	1.0334
50.0	0.146	1.1643
60.0	0.165	1.2174
70.0	0.240	1.3802
80.0	0.300	1.4771
90.0	0.390	1.5911
100.0	0.452	1.6551
110.0	0.565	1.7520
120.0	0.720	1.8573

Cont...

Time (min.)	O.D.	2 + log O.D.
130.0	0.899	1.9538
140.0	1.146	2.0591
150.0	1.790	2.2529
160.0	2.130	2.3284
170.0	2.352	2.3714

$k = 2.53 \times 10^{-2} \text{ min}^{-1}$

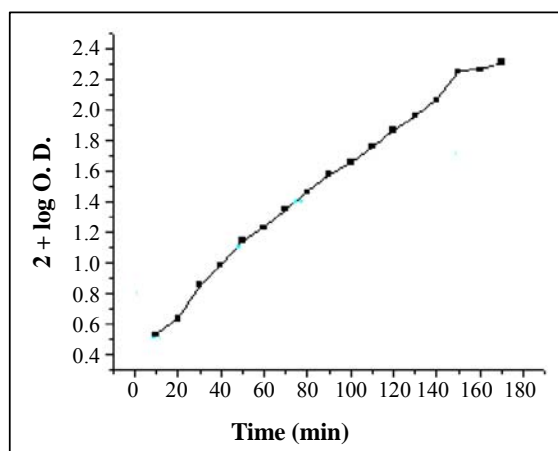


Fig. 1: A typical run

Effect of pH

The photochemical reaction of sodium nitroprusside in presence of dimethylurea (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 2.

Table 2: Effect of pH

[SNP] = 1.08×10^{-2} M	[Dimethylurea] = 1.89×10^{-3} M
$\lambda_{\text{max}} = 620$ nm	Light intensity = 21.0 mWcm^{-2}
pH	$k \times 10^2 (\text{min}^{-1})$
2.0	1.52
2.5	1.83
3.0	2.32
3.8	2.53
4.0	2.29
4.5	2.08
5.0	1.68
6.0	1.52
7.0	1.36
8	1.19

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 = 3.8. A decrease in the rate of 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 increase and hence, the reaction rate increases. But, on increasing the pH above 3.8, there is a possibility of a competitive reaction of ligand ions, DMU and 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, by keeping all other factors identical. The range of concentration was kept as between 0.80×10^{-2} M to 1.30×10^{-2} M. The results are reported in Table 3.

Table 3: Effect of sodium nitroprusside concentration

[Dimethylurea] = 1.89×10^{-3} M Light intensity = 21.0 mWcm^{-2}	
pH = 3.8 $\lambda_{\text{max}} = 620 \text{ nm}$	
[SNP] x 10^2 M	k x 10^2 (min ⁻¹)
0.80	1.53
0.85	1.76
0.90	1.96
0.93	2.08
0.98	2.27
1.00	2.36
1.08	2.53
1.12	2.32
1.14	2.27
1.20	2.05
1.25	1.98
1.30	1.89

It has been observed that the yield of the product of sodium nitroprusside with dimethylurea 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 increases; thus, resulting into a corresponding increase in the rate of reaction. After a certain limit, if the concentration of sodium nitroprusside was further increased, (i.e. above 1.08×10^{-2} M), there was a decrease in the rate of the reaction.

This decrease may be explained on the basis that the substrate is dark red colored, which will absorb a major part of incident radiations 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 dimethylurea concentration

The effect of concentration of dimethylurea on the rate of photochemical reaction of sodium nitroprusside was also observed by taking different concentrations of dimethylurea, keeping all other factors identical. The results are reported in Table 4.

Table 4: Effect of concentration of dimethylurea

[Dimethylurea] x 10 ³ M	k x 10 ² (min ⁻¹)
1.40	1.12
1.50	1.24
1.60	1.41
1.65	1.89
1.75	2.12
1.89	2.53
1.95	2.36
2.00	2.18
3.00	2.03
4.00	1.95
5.00	1.86
6.00	1.74

It was observed that as the concentration of dimethylurea was increased there was a corresponding increase in the rate of reaction, reaching a maximum at [Dimethylurea] = 1.89 x 10⁻³ M. It can be explained on the basis of the fact that the reaction rate increases due to an increase in the concentration of participating species. On the other hand, a decrease in the rate of reaction was observed on increasing the concentration of dimethylurea above 1.89 x 10⁻³ M. It may be attributed to the fact that higher concentration of dimethylurea 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 dimethylurea.

Effect of light intensity

The effect of light intensity 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 light source. The results are tabulated in Table 5.

The results given above 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 = 21.0 mWcm⁻²), no reasonable increase in the rate of reaction has been observed. On using higher intensities of light, 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. This point was shifted towards lower value, when vessels of smaller dimensions were used. A reverse trend was obtained with vessels of larger dimensions.

Table 5: Effect of light intensity

[SNP] = 1.08×10^{-2} M [Dimethylurea] = 1.89×10^{-3} M	
pH = 3.8 $\lambda_{\max} = 620$ nm	
Light intensity (mWcm^{-2})	$k \times 10^2$ (min^{-1})
14	1.87
16	2.12
18	2.30
20	2.38
21	2.53
22	2.53
24	2.53
26	2.53

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.

Analysis of the product

In neutral medium, the photochemical reaction between sodium nitroprusside and dimethylurea was carried out. It was observed that the initial light red color 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 residue was recrystallized with methanol giving green crystals of the product, which was analyzed as follows:

Elemental analysis

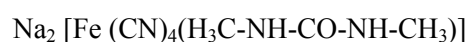
Element	Found (%)	Calculated (%)
Fe	19.00	19.05
C	28.55	28.57
N	28.57	28.57
H	2.75	2.72
Na	15.60	15.65
O	5.45	5.44

(ii) IR

A comparison of the IR spectra of the sodium nitroprusside, dimethylurea 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 670 cm^{-1} were found absent in the IR spectrum of the product.

The solid state IR spectra of dimethylurea and the metal complexes in the region 4000-400 cm^{-1} were compared and assigned on careful comparison. In the region 3450-3100 cm^{-1} , the N-H vibrations that appear as a broad peak at 3450 cm^{-1} in the spectrum of the ligand shifted to higher wave numbers in the complexes. The C-N bending vibration was at 1485.66 cm^{-1} in the spectrum of the complex. These shifts can be ascribed to increase in the double bond character of the C-N bond on complex formation. The infrared spectrum of the complex confirms that the dimethylurea ligand is coordinated to the metal ions via the oxygen atom with a reduction in the π -electron density of the exocyclic C=O bond. In addition, the $\nu_{\text{C=O}}$ bond of the free ligand is red-shifted to lower frequencies in the complex where as, the bending band of the methyl group in the product was found at 1375 cm^{-1} .

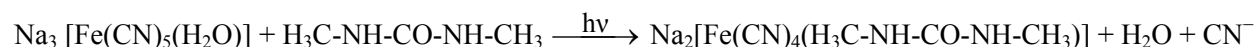
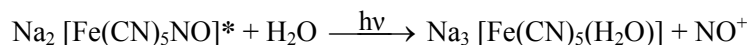
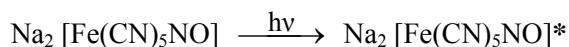
On the basis of the spectral and analytical data, the following tentative structure has been proposed for the compound.



In this case, dimethylurea ion behaves as a bidentate ligand.

Mechanism

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



Initially, the sodium nitroprusside is excited by absorbing incident radiations of a 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 favorable, because a neutral ligand like water (H_2O), can easily replace a cationic ligand (NO^+). Now, dimethylurea ion can easily throw water molecule out of the coordination sphere of iron. Sidewise a bidentate ligand (DMU) enters the coordination sphere of iron, replacing two CN^- ions. This is evident from the chemical analysis of the product.

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